Spatial and temporal trends in trace metal deposition in Canterbury, New Zealand.

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Abstract

Spatial and temporal trends in the deposition of lead, zinc, copper, cadmium and manganese in Canterbury, New Zealand, have been studied. The two main aspects of this study were an atmospheric deposition monitoring programme set up over the study area to assess present-day spatial trends; and an assessment of the ability of kahikatea tree ring wood to record historical trends in levels of heavy metals in the Christchurch atmosphere. The main instrumental technique used was atomic absorption spectrophotometry, with both flame and graphite furnace atomisation.

To study the dispersal of the metal-enriched aerosol from Christchurch, a network of deposition collectors was established over part of the Canterbury Plains. The main conclusions were that the rates of deposition of lead, zinc, copper and cadmium, but not manganese, showed an approximately exponential decay with distance away from Christchurch, and that the dispersion pattern was dependent upon the prevailing wind direction. It was also found that while rural deposition rates of zinc, copper and cadmium were lower than in other developed countries, the rates of lead deposition were similar to or higher than their overseas counterparts. Considerable seasonal variations in metal deposition rates tended to obscure an expected reduction in lead deposition fluxes following a reduction in the lead content of New Zealand premium grade petrol in July 1986.

Concentrations of lead, zinc, copper, manganese and cadmium were determined in the topsoils at the deposition collection sites, to assess the influence of atmospheric deposition on topsoil composition. Substantial differences, overriding the natural variability in soil composition, were found to exist between urban and rural soils. However, in rural sites, variations in metal deposition rates did not produce effects visible above natural variations, with the possible exception of lead.

To gain an historical perspective on the metal pollution history of Christchurch, the annual rings of kahikatea trees in Riccarton Bush, Christchurch, were analysed for lead, zinc, copper, manganese and cadmium. It was found that kahikatea trees appeared sensitive to environmental levels of these metals, showing accumulations of lead, zinc, copper and cadmium which appeared related to known historical emission trends. However, manganese concentrations in the ring wood appeared to be controlled by soil factors. A background stand of kahikatea trees showed no trends of increasing metal concentrations.

The use of peat deposits for historical monitoring purposes was also investigated. It was concluded that the only metals which appeared relatively immobile within the peat profile, hence indicating potential for recording historical trends in deposition fluxes, were copper and cadmium. The other metals appeared to have been mobilised by the severely anaerobic conditions in the bogs, as they were depleted below the permanent water table. However, deposition rates calculated in the surface peat were similar to fluxes measured by a conventional deposition collector at a similar site.

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Chapter 1

Introduction

1.1 BACKGROUND

Problems arising from the dispersal of metals into the environment are not new. The first human use of metals for the manufacture of tools, weapons and ornaments dates back to the Bronze Age, and during the period of the Roman Empire, mining of iron, gold, silver, tin, copper and lead was extensive. The expansion of the manufacturing industry during the Industrial Revolution brought about an increasing need for metals, which has continued into the 20th century (Purves, 1985).

The toxicity of metals to plants, animals and humans has been known for centuries, although it is probable that toxic effects due to either occupational or environmental exposure were frequently not recognized nor diagnosed at the time. Recently it has been suggested that the fall of the Roman Empire was in part due to endemic lead poisoning caused by the extensive use of lead-lined pots for cooking and storing wine (Gilfillen, 1965). Nriagu (1978) reports that the per capita consumption of lead was, at 4 kg/capita/year, quite comparable to the present-day American consumption of 6 kg/capita/year. Emsley (1986) has advanced the theory that the downfall of the British Empire may have also been related to the widespread use of lead. Other commonly-used metals with well-documented toxic effects are mercury, cadmium and arsenic (Purves, 1985; D'Itri and D'Itri, 1977; Nriagu, 1988).

However, it has only relatively recently been recognised that the mining of metals has produced disturbances to the natural biogeochemical cycles of these metals on a global

scale. In 1962, Chow and Patterson reported that approximately 50 times less lead had been leaving the oceans via pelagic sediments in prehistoric times than was reported by other investigators to be presently entering the oceans via rivers. The difference could be explained on a mass inventory basis as originating from industrial sources such as leaded gasoline exhausts and metal smelting operations, and this suggested that anthropogenic emissions might be interfering with the natural cycling of lead on a global scale. Later measurements by Patterson and coworkers actually revealed that the reports of lead concentrations in rivers were erroneously high, and the large excesses of lead were in fact entering the oceans by direct precipitation from the atmosphere.

Since 1962, Patterson and coworkers have demonstrated that enormous differences exist between present-day flows of lead through soils, water, air, plants and animals compared with those that had occurred during prehistoric times (Patterson, 1965; Murozumi, Chow and Patterson, 1969; Shirahata, Elias and Patterson, 1980; Ng and Patterson, 1981; Settle and Patterson, 1980, 1982; Elias, Hirao and Patterson, 1982; and Boutron and Patterson, 1983). The implications for human health of the greatly increased fluxes of these toxic metals and metalloids have been discussed by Patterson (1980), Purves (1985) and Nriagu (1988). Nriagu (1989) has summed up the seriousness of the situation by stating that "the annual total toxicity of all the metals mobilised exceeds the combined total toxicity of all the radioactive and organic wastes generated each year, as measured by the quantity of water needed to dilute such wastes to the drinking water standard."

A point that became obvious in the above studies was that the atmosphere, although small in mass compared with the other environmental reservoirs, is of vital importance in transporting metals from their sources to remote places. This is largely due to the dynamic, mobile nature of the atmosphere.

Several authors have estimated and compared anthropogenic and natural contributions to the total atmospheric burdens of trace metals. Natural sources of metals to the atmosphere are considered to include windblown dust and soil; volcanic emissions; forest fires and vegetative exudates; and seasalt sprays, whereas anthropogenic sources of metals arise mainly from high-temperature processes such as fossil-fuel combustion and

metal smelting operations. It should be pointed out that this approach is beset with practical difficulties due to uncertainties in both the quantity of aerosols released from each source, and the emission factor applicable to each process. This is particularly true for episodic processes such as volcanic eruptions.

Lantzy and Mackenzie (1979) calculated "mobilisation factors" for 16 trace metals, where the mobilisation factor is defined by the anthropogenic emission rate divided by the natural emission rate. Mobilisation factors obtained by Lantzy and Mackenzie for lead, zinc, copper, manganese and cadmium are presented in Table 1.1, together with figures obtained by Nriagu and coworkers.

Table 1.1 Ratio of anthropogenic to natural emissions of trace metals to the atmosphere

Element	Lantzy and Mackenzie(1979)	Nriagu (1979)	Nriagu and Pacyna (1988)	Nriagu (1989)
Pb	340	18	17	28
Zn	23	7.2	2.9	2.9
Cu	14	3.0	1.9	1.3
Mn	0.52	-	0.074	0.12
Cd	19	8.8	7.6	5.8

It is clear from a discussion by Nriagu and Pacyna (1988) that the mobilisation factors obtained by Lantzy and Mackenzie are artificially high. This is because Lantzy and Mackenzie have assumed, incorrectly, that 90% of the metal concentrations in coal and oil are released to the atmosphere whereas in fact pollution control strategies have produced much lower emission factors. Lantzy and Mackenzie have also excluded the very important automobile exhaust contribution to global lead emissions.

The data presented by Nriagu and Pacyna (1988) is a revised and expanded version of the data presented in Nriagu (1979). It is evident that the estimates of the ratios of anthropogenic to natural emissions have declined slightly in the later paper; this is mainly due to the overall global reduction, between 1975 and 1983/84, in the emission of particulates by industries and the phasing-out of the consumpion of leaded gasoline.

Nriagu (1989) has further refined the assessment of natural sources of atmospheric trace metals, and reported that the biogenic contribution is more important than previously thought, particularly for copper and cadmium. Thus, the anthropogenic

to natural emission ratios of these metals have been revised downwards. However, the ratio for lead has been revised upwards.

It is very evident that anthropogenic emissions of metals to the atmosphere have had a large impact on the aerosol composition in populated, industrialised regions of the world (e.g. Rahn, 1976; Gordon, 1980, Chow and Earl, 1970, Janssens and Dams, 1975). When one leaves the urban scale of pollution and looks at larger regions, the impact of anthropogenic emissions can still be easily observed (Zoller, 1984). An example of this type of problem is the acid deposition experienced in the North Eastern United States and Canada, as well as Scandinavia and Europe (e.g. Likens et al., 1979). However, the possibility of transport of metal-enriched aerosols to regions of the earth remote from anthropogenic emission sources is less well understood, and has been the subject of intensive investigations for the past two decades.

Most of these investigations have focussed upon analyses of aerosol and snow and ice samples from the remote North and South Polar regions, to detect any anthropogenic perturbances. As it has been shown that the chemical composition of the deposited snow and that of the low-altitude atmospheric aerosols are closely related (Boutron and Lorius, 1979; Davidson et al., 1981; Maenhaut et al., 1979), measurements of chronological variations preserved in successive snow layers provide historical records of the chemical composition of the aerosol.

It should be pointed out that much confusion has surrounded the analysis of aerosol and snow samples from remote locations. Due to the extremely low levels (in the 10^{-12} g/g range for many metals) in remote samples, problems of contamination during sample collection, handling and analysis are severe and many published results are of dubious validity. Much of the credit for reliable data is due to Patterson and coworkers, who were among the pioneers of techniques for ultraclean analysis (summarised in Patterson and Settle, 1976).

In 1969, Murozumi et al. analysed snow layers from Greenland and Antarctica and reported a 200-fold excess of lead in recent Arctic snow that could not be accounted for by windblown dusts. This excess of lead was claimed by these authors to arise from recent anthropogenic emissions, on the basis of historical trends in the lead

concentrations, which were found to coincide with the historic increase of lead production and atmospheric emissions. However, there have been controversies between Patterson's group and others (e.g. Herron et al., 1977; Weiss et al, 1978) regarding the occurrence of lead in ancient Arctic ice and on the variations of lead concentrations from preindustrial times to the present. These controversies were resolved by Ng and Patterson (1981) who showed that the data obtained by the above-mentioned authors was in high positive error because of the failure of these authors to overcome contamination introduced during coring of the ice. Ng and Patterson detailed a procedure where successive veneers of the ice were removed and analysed, so a concentration profile extending to the centre of the core could be obtained. If the concentrations continued to decrease to the centre of the core, an upper concentration only could be assigned.

Thus, there is now general agreement that this 200-fold excess of lead in modern Arctic ice is related to increased anthropogenic emissions to the atmosphere in the Northern Hemisphere. This conclusion has been supported by evidence of increased lead fluxes to other remote Northern Hemisphere locations (e.g. Chow et al., 1970; Shirahata et al., 1980; Settle and Patterson, 1982; Ng and Patterson, 1982).

However, for other metals, there is little or no evidence of increasing concentrations in the Greenland ice cap, with the possible exception of zinc (Boutron, 1986). This lack of a clear increase is surprising, as it is not consistent with global inventories (discussed previously) of natural and anthropogenic emissions of metals, which indicate that for some metals, notably lead, zinc and cadmium, the current anthropogenic fluxes largely exceed natural rates in the Northern Hemisphere and have strongly increased since last century.

It is also surprising because studies of the Arctic aerosol (summarised by Heidam, 1986) have shown that the aerosol has a very pronounced annual cycle, with high concentrations of many metals, as well as soot and sulphur, in winter. The annual variations are ascribed to fluctuations in the position of the Polar front. In winter, the front lies to the south of industrialised regions, which become part of the Northern air mass. Factor analyses of the aerosol composition also point towards anthropogenic sources (Rahn, 1981).

Hence, in view of these considerations, it appears likely that future work will show the presently observed lack of evidence for increasing metal (other than lead) concentrations in Arctic ice to be due to unreliability of the data, particularly for old ice.

For Antarctic snows, a recent analysis by Boutron and Patterson (1983) of ultraclean samples covering the past two centuries showed that most previously published data were in high positive error. It appears that surface Antarctic snows have lead concentrations in the range of 1 to 5 pg g^{-1}, which are similar to concentrations of 1 to 2 pg g^{-1} lead reported in ancient Antarctic ice (Ng and Patterson, 1981). Boutron and Patterson interpreted these data as indicating a possible 2 to 3-fold increase over prehistoric levels. However, much remains to be understood about natural variations in the prehistoric lead flux. Boutron (1980) speculated that volcanic activity may produce the observed fluctuations, but this theory was later shown to be based upon erroneous data (Ng and Patterson, 1983).

More recent work by these authors (Boutron and Patterson, 1986; Boutron et al., 1987) has showed that natural concentrations of lead in ancient Antarctic ice have varied widely, reaching concentrations of 30 pg g^{-1} during the Last Glacial Maximum and declining to very low concentrations of 1 pg g^{-1} during the Holocene. Calculation of lead:aluminium ratios have shown that the prehistoric lead flux was controlled mainly by wind-entrained soil particles, although up to 50% of the lead may have been of volcanic origin during the Holocene.

For the other metals, studies to date have not reported increasing trends in concentrations over the past century (Boutron, 1986). However, the reliability of these studies is not as well-established as for lead, as less attention has been focussed upon the other metals. A recent study (Batifol et al., 1989) of variations in zinc, copper and cadmium concentrations during the past 40,000 years in fact reports lower concentrations than those summarised in Boutron (1986). This was particularly evident for cadmium. For 12,000 year old ice, a value of 2.6 pg g^{-1} Cd was reported by Boutron et al. (1984); this is approximately an order of magnitude higher than a range of values of <0.1 to 0.66 pg g^{-1} for ice 11,000 to 14,300 years old reported by Batifol et al. This suggests that earlier data for zinc, copper and cadmium may be in positive error.

In conclusion, no significant increases have been observed in Antarctic snow layers for the investigated metals, which is in good agreement with the facts that the bulk of anthropogenic emissions occur in the Northern Hemisphere (Nriagu, 1978), and that interhemispheric aerosol transport is inefficient. This does not imply, however, that the Antarctic data are reliable.

Hence in summary, there is clear evidence for long-range transport of metal-enriched aerosols of anthropogenic origin in the Northern Hemisphere. However, in the Southern Hemisphere, the most remote location (the Antarctic ice cap) appears much less affected by anthropogenic emissions of trace metals.

1.2 THE NEW ZEALAND SITUATION

Studies that have investigated the dispersal of metals of anthropogenic origin from their sources in the New Zealand environment will be briefly reviewed in this section.

The dispersal of metals on a local scale is well-documented. Elevated levels of heavy metals have been reported in soil, roadside dusts, vegetation, aerosol samples and river sediments in the major cities of New Zealand (e.g. Day, 1977; Fergusson et al., 1980; Fergusson and Simmonds, 1983; Fergusson and Ryan, 1984; Collins, 1984; Graham, 1984). Emissions from specific sources have also been studied. In particular, the high concentration of lead in New Zealand petrol has caused concern about the dispersal of this metal into the environment (Royal Society of New Zealand, 1986).

Lead, in the form of tetra-alkyl derivatives, has been used for over 60 years as a petrol additive to enhance the octane rating. Up until July 1986, the lead content of Premium grade motor fuel was 0.84 g l^{-1}, which rated as one of the highest levels in the world. After this date, Premium grade petrol was reduced to 0.45 g Pb l^{-1}, which is still one of the highest levels among developed countries. In January 1987, a grade of unleaded fuel became available.

Expressed on a land-area basis, the total rate of dispersion of lead per unit area is much smaller than for the USA or Britain, mainly because of the sparse population of New Zealand. However, lead usages in the major cities are more comparable to overseas cities, and it has been estimated that petrol-derived lead is dispersed in the major New

Zealand cities at rates comparable with those for cities such as Chicago or Turin. Aerosol lead concentrations in Christchurch (Simmonds and Fergusson, 1983) and Auckland (Graham, 1984) consistently exceed safety limits set in Europe and the USA. Studies have shown that that roads are line sources of lead pollution, both in cities (Fergusson and Simmonds, 1983; Collins, 1984; Day, 1977; Ward et al., 1974; 1977b; 1977c) and away from cities (Ward et al., 1975a; 1975b; Collins, 1988). It has also been reported that zinc, copper, nickel, chromium and cadmium originate from traffic (Ward et al., 1977b; Fergusson et al., 1980).

New Zealand is not a highly industrialised country, but the dispersal of metals from industrial activities has produced very highly elevated concentrations of metals on a local scale. For instance, Ward et al. (1976) found that dispersal of lead, zinc, copper and cadmium from a base-metal mine produced very high concentrations in soils, stream sediments, waters and natural vegetation, severely affecting an area extending several hundred metres from the mine. However, the mine had been abandoned in 1973 after a decade of mining, and Ward et al. (1977a) found that surface metal concentrations had diminished appreciably over a period of a year. Ward et al. (1977c) found that although emissions from a lead battery factory and smelter in Auckland produced extremely high concentrations of lead in topsoil in the smelter grounds, at a distance of 90m from the smelter the concentrations of topsoil lead were dominated by traffic exhaust emissions.

The dispersal of metals into the New Zealand aquatic environment has been quite widely studied (summarised in Smith, 1986), mostly due to concern about water quality. Analyses of sediments and biota have been used to assess the exposure of waters to metal discharges. Smith (1986) reported that the sediments in harbours, estuaries and rivers associated with the four main cities in New Zealand show elevated concentrations of heavy metals. The most severe case is considered to be in Wellington, where extremely high concentrations (of up to 146,000 μg/g Pb), have been found in the sediments of Waiwhetu Stream. This stream flows through a heavily industrialised part of Lower Hutt, including a battery factory, a car assembly plant, a paint factory, and electroplating industries. In Christchurch, Purchase and Fergusson (1983) found that the sediments of the Heathcote River, which flows through an industrialised region of Christchurch, were

highly polluted with lead, antimony and chromium, and moderately polluted with zinc, cadmium and copper, due to effluent discharges from a lead battery factory, a rubber manufacturing plant, and several tanneries along the banks of the river.

There are also reports of elevated metal concentrations in the sediments of Manakau Harbour (Auckland); Wellington Harbour and Otago Harbour (Dunedin), usually attributed to specific sources such as urban runoff, fertiliser works, iron and steel works, tanneries, sewage outfalls and wharf activities.

Another well-documented example of elevated metal concentrations is the discharge of arsenic into the Waikato River. Aggett and Aspell (1980) reported that arsenic, released to the river by both natural enrichment in geothermal fluids and discharges from the Wairakei geothermal power station, is absorbed in the sediments of the artificial hydro-lakes. Reay (1973) estimated that the Wairakei Power Station provides approximately 75% of the total arsenic input to the river system, with the remainder being naturally mobilised.

In summary, it can be concluded that there are numerous sources mobilising metals into the New Zealand environment. Hughes (1985) has placed some perspective on the situation by stating that current priority issues of environmental concern are the discharge of metals and metalloids (mostly arsenic and mercury) from natural geothermal systems and geothermal energy developments; effluent discharges from petrochemical industries; leachates from mining operations; and the dispersal of lead from leaded petrol combustion.

Very few studies have investigated the transport of heavy metal pollutants beyond the immediate locality of their sources. As indicated previously, most studies have concentrated on analyses of environmental materials in areas where the effects of some source of metal pollution could be reasonably expected to be evident.

Surface waters, because of their naturally low metal content, would be expected to be sensitive indicators of atmospheric deposition. There are numerous reports of water composition in estuaries, rivers and lakes over the whole of New Zealand (summarised in Smith, 1986). However, analyses of New Zealand freshwaters using ultraclean techniques (Tunnicliffe and Beaumont, 1986; Ahlers and Hunter; 1986; 1988) have

shown that it is very probable that most of these previous studies failed to overcome contamination problems. Certainly, many of the studies summarised by Smith (1986) report detection limits that are orders of magnitude higher than the baseline concentrations reported in pristine freshwaters by Ahlers and Hunter (1986; 1988), who have studied the chemistry of a remote Central Otago river over a seven-year period. Using ultraclean techniques, these authors have reported that concentrations of both major ions and trace metals are extremely low by world standards. For example, lead concentrations in the headwaters of the river are in the range 5 to 30 pg g^{-1}, compared with 1 to 5 pg g^{-1} reported for Antarctic snows. Other measurements (quoted in Ahlers and Hunter, 1986) for freshwater concentrations in other remote parts of New Zealand suggest that these waters are similarly unaffected by anthropogenic emissions. A slightly higher range of concentrations of 15 to 120 pg Pb g^{-1} for the Waikato river is thought to be due to natural enrichment from geothermal activity (Smith, 1986).

Thus, very little is known about the longer-range transport of metallic pollutants. Ward et al. (1975b) studied the distribution of lead in roadside soils and vegetation along a remote, low traffic volume highway in the central North Island. These authors reported that just over half the total emitted lead was found to be contained in the soil within 250 m of the road and 6 cm of the surface. Thus, the remainder had been transported from the locality. A recent relevant study was that of Collins (1988) who measured lead deposition throughout a catchment in Dunedin with low-to-moderate traffic density. It was reported that the lead deposition rates ranged from in excess of 10,000 $\mu g/m^2/day$ beside a steeply inclined road with a traffic volume of 5,000 vehicles day^{-1}, to 80-100 $\mu g/m^2/day$ in the backyards of homes adjacent to roads with traffic volumes of 4,000 vehicles day^{-1}, to a reported background of 5 $\mu g/m^2/day$. The effect of roadways appeared to dominate the spatial distribution of the lead fluxes. However, reservations must be expressed about the methodology used in this study. The author reports a procedural blank of 66 $\mu g/m^2/day$, which is very substantial compared to reported fluxes further away from roadways. Also, since no indication is given of the variability in the blank, the practice of subtracting this blank from the raw data appears dubious.

A final point is that the background aerosol in New Zealand may be influenced by upwind sources. Holden and Clarkson (1986) addressed this question in relation to sulphur dioxide emissions, noting that the position of New Zealand in relation to Australia is analogous to the position of Scandinavia downwind of the United Kingdom. These authors calculated, from emission data and an atmospheric transport model, that approximately twice as much sulphur dioxide is deposited on New Zealand from sources along the East Coast of Australia than from indigenous sources.

A related study was made by Steiner and Clarkson (1985), of the lead content of New Zealand offshore precipitation. These authors reported that rainfall from airmasses which had originated over the Southern Ocean contained 17 pg Pb g^{-1}. In contrast, a rainfall sample collected in the mid-Tasman from an airmass that had originated over Australia contained 490 pg Pb g^{-1}. This suggests that Australian sources may have some effect on ambient lead concentrations in New Zealand.

1.3 OUTLINE OF THIS STUDY

The study area in this thesis consisted of the city of Christchurch (population approximately 300,000) and the Canterbury Plains, which extend for approximately 80 km to the west. To the east, the city is bounded by the sea, and to the southeast, by the hills of Banks Peninsula.

The area was considered to be a suitable size for studying the dispersal, on a regional scale, of heavy metals mobilised into the atmosphere by sources concentrated in the Christchurch urban area. This was achieved by installing a network of deposition collectors to measure spatial patterns of heavy metal deposition across the study area. Metal deposition was monitored over a two-year period to allow seasonal trends to be investigated. The elements chosen for study were lead, zinc, copper, manganese and cadmium. The metals lead, zinc, copper and cadmium have been found to be elevated in the Christchurch environment (e.g. Fergusson and Ryan, 1984); whereas manganese, which arises mainly from soil, was used as a reference element. It was also of significance because many metals are associated with iron-manganese oxides in soils, sediments and peats.

As an extension of this study, the metal concentrations were determined in the topsoils at the deposition sites, to investigate the influence of atmospheric deposition in topsoil composition. It is well-established (Purves, 1985) that urban soils are strongly modified by anthropogenic additions, but effects on rural soils are less well understood.

The second main aspect of this study was an investigation of two historical monitoring techniques. Historical (or retrospective) monitoring is the analysis of environmental materials which have been deposited in discrete or identifiable layers, and which are capable of retaining a record of environmental conditions existing during deposition. The main environmental materials of value in historical monitoring are polar ice and snow layers (discussed in Section 1.1), sediments, peat deposits and tree rings. MARC Report 31 (1985) is a recent, comprehensive review of this whole subject.

Ice and snow cores are usually used to monitor atmospheric changes in remote areas. The information obtained from such cores is unambiguous, because they are derived entirely from precipitation. However, ice and snow are extremely difficult to analyse due to their low metal concentrations, and there are many erroneous data in the literature.

The most extensive historical database exists in the sedimentary record. Sediments contain fine-grained particles, suitable for pollutant fixation, such as clay minerals, Fe/Mn oxides, and humic substances. Lake, estuarine and coastal sediments have been found to retain a record of local effluent input, which usually outweighs direct atmospheric deposition. However, offshore marine basin sediments have been used to monitor long-range transport of airborne pollutants (e.g. Ng and Patterson, 1982).

Cores obtained from tree rings and peat bogs are generally the most difficult to interpret, because trees are living organisms and peat is chemically very active. However, there is sufficient evidence to indicate that both tree rings and peat bogs can record local pollution histories for a number of metals.

To gain a historical perspective on the metal pollution history of Christchurch, possible environmental materials located in or near the city are estuarine and river sediments, and tree ring wood.

The sediments of the Avon and Heathcote rivers, and of their estuary, have been thoroughly investigated by researchers at the University of Canterbury, and the Christchurch Drainage Board. In general, it appears that the sediments of the Avon-Heathcote estuary do not accumulate heavy metals. Purchase and Fergusson (1986) found that high concentrations of lead, antimony and chromium in the lower Heathcote river (from effluent discharges) were not also present in the estuarine sediments. This is thought to be due to three effects : dilution of sediments in the larger volume of the estuary; strong fixing of pollutants to the river sediments, thus restricting their mobility; and rapid erosion of estuarine sediments into the ocean. However, the rapid erosion rate, considered to be a product of urbanisation (Macpherson, 1979), is thought to be slowing down. Deely (1988) has reported a four-fold enhancement of metals in modern Avon-Heathcote sediments relative to ancient estuarine deposits elsewhere in Canterbury, and considers that this enhancement is most likely related to industrial activity.

The other possibility for historical monitoring of the Christchurch environment is the analysis of tree ring wood. A previous attempt by Fergusson et al. (1980) to correlate lead concentrations in the ring wood of a 90 year old lime *(Tilia europea)* tree from a busy urban roadside with traffic emissions was not successful. However, it is likely that as lime trees are hardwoods, the well-developed rays which are thought to be an excretion route for toxic products may have transported lead to the inner ring wood. Certainly the reported concentrations of lead in the ring wood (2.7 to 4.9 $\mu g\ g^{-1}$) are much higher than those found in the inner ring wood of the kahikatea trees analysed in this study ($\approx 0.2\ \mu g\ g^{-1}$).

Kahikatea trees were considered to be very suitable for historical monitoring purposes, because of their softwood structure, and also because of their large lifespan. The stand of trees sampled for this study were approximately 350 years old, which enabled the pre-European period in Canterbury to be studied.

It was also decided to investigate the potential of peat deposits for historical monitoring purposes. Three peat bogs were studied, located in inland Canterbury. In particular, it was hoped to obtain rates of atmospheric metal deposition for comparison

with deposition measured by a collector placed at a similarly remote site as part of the deposition monitoring network.

In addition to the work described above, which is discussed in Chapters 3 to 6 of this thesis, Chapter 2 deals with the question of quality assurance of data, which was considered to be an essential part of this study, and Chapter 7 covers general experimental techniques used throughout this study.

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Chapter 2

Quality assurance

A basic question that must be addressed in an analytical study is whether data produced are reliable and acceptable. Throughout this study, emphasis was placed upon the evaluation of data quality.

2.1 INTRODUCTION

2.1.1 General principles

A quality control system is the basis for having confidence that a measuring system is producing meaningful data, that is, data of well-established accuracy and precision. The terms accuracy and precision need explanation. Precision refers to the variability or 'spread' of individual measurements whereas accuracy refers to the absence of bias or closeness of these measurements to the true value. Cali and Reed (1976) and Kirchmer (1983) point out that accuracy cannot be established until good precision is achieved; hence the first step in quality control is to attain reproducibility in the measuring process (Taylor, 1981). This means that sources of imprecision should be identified and minimised as far as possible. For instance, in graphite furnace atomic absorption spectrophotometry, precision may be improved from ±10% to ±5% by replacing the manual injection of 2 μL aliquots into the furnace with an autosampler. While the effect of random error is minimised by replication there are practical limitations imposed by time and resources. Once satisfactory precision has been achieved, tolerance limits may be set

beyond which data may confidently rejected as outliers. The measurement system is said to be in a state of statistical control.

Once stability in the measurement process has been demonstrated, accuracy can be assessed. This is usually carried out by the analysis of standard reference materials(SRMs). A SRM is a substance well-characterised with respect to one or more of its properties or constituents, produced and distributed in quantity for accuracy assessment purposes. Geological SRMs have been available since 1901 and more recently a wide range of environmental and biological standards have been produced. Muramatsu and Parr (1985) review those available in 1985. Many authors have discussed the role of SRMs in trace analysis (Cali and Reed, 1976; Cali et al, 1975; Taylor, 1981; Ihnat, 1988). The SRM is subjected to the measuring process in question and the values obtained compared with certified values to determine the accuracy of the process. If there is a statistically significant difference, a bias exists and must be corrected.

Once the experimental mean of a measuring process is statistically acceptable, the analyst may proceed to the analysis of 'real' samples with the following provisos. For correct measurement of a SRM to imply correct measurement of real samples, it is necessary for a) the SRM to be as close as possible to the real sample in both the nature of the matrix and the concentration of the analyte and b) no special care to be taken in the analysis of the SRM, compared with actual samples.

A potential problem in the use of SRMs to establish accuracy is related to the observation that many analysts obtain better results when the correct value is known to them (Byrne, 1976). It seems that an unconscious bias towards the true value may be operating. To overcome this, it is preferable to include SRMs with real samples in an anonymous, random fashion.

The continued surveillance of quality over time is another important function of reference materials. Primary (SRM) and secondary standards will both serve this purpose. A plot of measurement data against time will enable the analyst to detect any deterioration in quality due to time-dependent phenomena such as instrument drift or deterioration in standard solutions.

2.1.2 Quality control in this thesis

In practice, it was not always possible to apply the principles outlined in Section 2.1.1. Because it is expensive and difficult to produce and certify SRMs (Zief and Mitchell,1976), it is not always possible to obtain ideal SRMs and use must be made of available ones. The SRMs analysed for the elements lead, zinc, copper, manganese,cadmium and calcium in the course of this work were IAEA Soil-5, Marine Sediment SD/N/1-2, Air Filter 3/1, Cotton Cellulose V-9 and Hay Powder V-10. Thus the range of real environmental samples encountered in this work were adequately covered. Details of the analytical methods developed will be given in separate sections. The usual approach was to devise alternative methods based on equipment and instrumentation available, and to test the accuracy of these methods against suitable SRMs. Some modification was frequently necessary.

2.1.3 Statistical treatment of data

The extent of statistical treatment of the data was determined by the information provided by the certifying body (in this case, the International Atomic Energy Agency) and will be discussed in more detail for each SRM analysed. Generally, certified data took the form of a concentration value with a 95% confidence interval (C.I.), but with little information about the underlying distribution or how the 95% C.I. was calculated. This information is based on the results of an intercomparison run, and the I.A.E.A. recommend that the overall median of the laboratory means provides the best measure of the true concentration.

If the experimental mean lies outside the certified 95% C.I., it can confidently (α=0.05) be rejected as biased. If it lies within the interval there is no basis for rejection, and the experimental mean is acceptable.

2.1.4 Additional indicators of data quality

Other indicators of data quality which are not definitive in themselves but which can provide additional confidence are comparisons of results obtained by independent measuring processes, and by other analysts. These will be discussed in Sections 2.3 and 2.4.

2.2 ANALYSIS OF STANDARD REFERENCE MATERIALS

2.2.1 Air filter 3/1

This synthetic reference sample consists of quantitative filter papers (Macherey Nagel MN 0.45 μm, ø=5.5 cm) spiked with 20μL aliquots of a solution containing 17 trace elements plus some elements usually present as major components of dust (Al, Ca, Mg, Na and K). The composition of the solution was adjusted to give relative proportions of metals similar to typical airborne particulate matter. A set of unspiked filters was also provided to allow measurement of the blank contribution by the filter paper.

Although the method adopted for dustfall collection in this thesis did not make use of air filters but relied on a sedimentation technique, it was thought that the reference material would be similar enough in chemical composition to provide a useful measure of accuracy. Hence, the method used for the analysis of dustfall was tested out on the spiked filters. For urban dustfall, digestion with 4M HNO_3 gives adequate recovery of heavy metals as the metals are present in extractable forms (Fergusson and Ryan, 1984). However dustfall in remote regions contains more crustally derived materials and digestion using the strong acids HF and $HClO_4$ are necessary to recover metals from silicate minerals, and oxidise any organic matter.

The filter papers were transferred in the Clean Room from their protective polyethylene bags to preweighed platinum crucibles. These samples were dry-ashed in a muffle furnace, keeping the temperature below 430°C to avoid reported losses of volatile species (Webber, 1972). The ash was digested with 6 ml conc. HF(Analar grade) and 3 ml conc. $HClO_4$ (Analar grade). This treatment was repeated until a white residue was obtained; this was taken up in 10 ml 2M Analar HNO_3.

The metals lead, zinc, copper, manganese and cadmium were analysed by flame atomic absorption spectrophotometry (FAAS). The digested blank filters were analysed by graphite furnace AAS (GFAAS) and found to contribute <1% to the analytical signal in all cases. The instrumental parameters used for AAS are set out in Table 2.1. Instrumental analysis will be discussed in greater detail in Chapter 7.

A summary of results for the FAAS analysis of Air Filter 3/1 are presented in Table 2.2, together with certified data (IAEA/RL/95, 1982). Terms in Table 2.2 (and subsequent tables) that need definition are X (the experimental mean), s (the experimental standard deviation) and N (the number of independent determinations).

Table 2.1 Instrumental parameters for atomic absorption spectrophotometry

Element	Wavelength (nm)	Lamp current (mA)	Slit width (nm)	Background Correction
Cd	228.8	4.0	0.5	ON
Cu	324.8	3.0	0.5	OFF
Mn	279.5	5.0	0.2	ON
Pb	217.0	5.0	1.0	ON
Zn	213.9	5.0	1.0	ON

Table 2.2 Air Filter 3/1

	Experimental data			Certified data	
Element	N	X (μg/filter)	s	Content (μg/filter)	95% C.I. (μg/filter)
Cd	4	10	1	10	9 - 11
Cu	4	44	5	46	42 - 49
Mn	4	27	2	30	28 - 32
Pb	4	107	6	105	95 - 112
Zn	4	145	5	143	132 - 152

Thus, $HF/HClO_4$ digestion of the synthetic filters followed by FAAS analysis produces acceptable results for lead, zinc, copper and cadmium. The mean concentration for manganese was slightly biased on the low side.

2.2.2 Marine sediment SD/N/1-2

This SRM is a natural marine sediment from the North Sea; its mineral composition is approximately 60% quartz, 20% calcite, 10% clay, 6% feldspar, 3% NaCl and 1-2% pyrite. A comprehensive report exists (I.A.E.A. RL/124) of the intercomparison run that formed the basis of the certified data.

SD/N/1-2 was available in quantity; hence it was analysed many times during the course of this work. Although sediments were not studied extensively during this work, sediment is similar in composition to both soil (with a much lower organic content) and crustally derived dustfall.

To achieve complete dissolution of the silicate minerals, conc. HF/HNO_3 (5:1) was added to dry-ashed 1 g subsamples of SD/N/1-2. The mixed acids were fumed off and the treatment repeated until a white residue remained. This residue was taken up in 25 ml 2M HNO_3.

Analyses were carried out by FAAS for lead, copper, zinc and manganese and by GFAAS for cadmium. Results are presented in Table 2.3, together with certified data.

Table 2.3 Marine sediment SD/N/1-2

	Experimental data			Certified data	
Element	N	X (μg/g)	s (μg/g)	Content (μg/g)	95% C.I. (μg/g)
Cd	20	10.8	0.3	11.0	10.0 - 12.0
Cu	20	72.4	3.7	72.2	68.1 - 75.2
Mn	20	648	21	777	728 - 801
Pb	20	121	10	120	112 - 132
Zn	20	425	13	439	423 - 452

It can be seen from the above tables that a total HF/HNO_3 digestion produces experimental means that lie within the certified 95% C.I. for cadmium, copper, lead and zinc but well below for manganese. Hence it must be accepted that the mean for manganese is biased as only ≈83% is recovered by this procedure.

The possibility of atomic absorption matrix effects causing a depression in manganese absorbance was investigated by using the technique of standard additions. However, results obtained by this procedure were found to be very similar to those obtained without the use of standard additions. Hence, the low value for manganese recovery is probably due to incomplete dissolution of manganese oxides. However, the coefficient of variation is small for manganese analysis (3.2%) over 20 determinations and it was assumed that an accurately known proportion of manganese is recovered, and that this will also hold for material of similar composition. For material with a higher

organic content, it would probably be advisable to use $HClO_4$ to ensure complete dissolution.

2.2.3 Soil-5

This SRM is a topsoil from Peru; it was a useful material on which to test soil extraction procedures used in this work. To determine total concentrations of metals, a total extraction using 1:1 40% HF/conc.HNO_3 was performed. This procedure is recommended by Harrison and Laxen (1977) for the complete recovery of lead from soils. Using polypropylene beakers, 0.2 g subsamples of Soil-5 were digested with 20 ml of HF/HNO_3. The solution was evaporated to dryness and the residue taken up in 2M HNO_3 and analysed by FAAS for lead, zinc, copper and manganese and by GFAAS for cadmium. The results, together with certified data, are listed in Table 2.4.

Table 2.4 Soil-5

	Experimental data			Certified data	
Element	N	X (μg/g)	s (μg/g)	Content (μg/g)	95% C.I. (μg/g)
Cd	8	1.47	0.05	1.5	-
Cu	8	73.0	3.1	77.1	72.4 - 81.8
Mn	8	701	14	852	815 - 883
Pb	8	130	6.6	129	103 - 155
Zn	8	355	5	368	360 - 376

The data listed in Table 2.4 show that the HF/HNO_3 extraction produces acceptable values for lead, copper and cadmium but a low recovery (≈82%) of manganese. This recovery is very similar to the recovery of manganese from sediment SD/N/1-2 and again is probably due to incomplete dissolution of manganese oxides. The zinc recovery is slightly low (≈96%) and this may be due to zinc occluded in the manganese oxides.

An extraction using 4M HNO_3 was also performed upon Soil-5. It was found that its efficiency was only slightly less than for the HF/HNO_3 treatment. Hence, due to its greater convenience, it was used routinely for digestion of soil samples. The precision of the 4M HNO_3 digestion was assessed by repeated analyses of internal standards (Section 2.4).

2.2.4 Cotton cellulose V-9 and hay powder V-10

These biological SRMs will be discussed in the same section as they have very similar compositions and were treated in the same manner. The correct measurement of metals in these woody materials is much more difficult than the soils and sediments already described; this is because the total metal contents are low (for example, the cadmium content of cotton cellulose is only 0.002 μg/g compared with 11 μg/g in the marine sediment) and the matrix consists of >99% cellulose and lignin. The complete and contamination-free removal of this organic matrix is the critical analytical step. Sansoni and Panday (1981) review ashing methods applicable to biological trace analysis.

Destruction of cellulose and lignin involves breaking down chains of carbon atoms into single-C units which may be easily oxidised to CO_2. The energy required to break C-C bonds can be supplied as heat (as is the case in classical dry ashing), or oxidation may proceed via a free radical initiated pathway. Several ashing methods were tried, and compared.

The simplest method, dry ashing, was carried out by heating 0.2 g subsamples in a muffle furnace until a white ash remained(usually 16-20 hours). The main disadvantage of this technique is the possibility of losses of volatile analyte species at high temperatures (Webber, 1972). It was found that if the temperature was kept below 430° losses were not significant.

Wet-ashing usually involves digestion of 0.1-1.0 g subsamples with combinations of the strongly oxidising acids HNO_3 and $HClO_4$; and also H_2SO_4. The addition of H_2O_2 is also recommended, to initiate free-radical cleavage of the carbon chains. In this study, two such methods were investigated.

In the first treatment, which was reported as successful in the digestion of hair samples (Fergusson et al., 1981), aliquots of 2 ml 16M HNO_3 plus 0.3 ml 30% H_2O_2 were added to 0.2 g samples of cotton cellulose. The mixture was gently evaporated to dryness and the treatment repeated until a white residue appeared. The second treatment consisted of 5 ml 16M HNO_3 plus 1 ml 10M $HClO_4$. The main disadvantages of wet ashing are the explosion hazard associated with perchloric acid, and the potential for

contamination from the large volumes of added reagents. This was a particular problem for H_2O_2. Also, the fuming off step was prone to airborne contamination.

The third technique investigated was low-temperature oxygen plasma ashing. The Tracerlab 500 low temperature asher in the Geology Department of the University of Canterbury has been used successfully for ashing coal (N. Newman, pers. comm., 1987). Activated oxygen plasma is produced from O_2 passed through a radiofrequency field and contains "a mixture of atomic and ionic species as well as electronically and vibrationally excited states" (Gluskoter, 1965). Ashing takes place below 200°C because of the free radical mechanism; gaseous oxidation products are removed by vacuum. The main problem with this technique was that it was very slow as complete ashing took over a week.

The ashing products from all the above trial procedures were taken up in 2M HNO_3 and analysed by AAS. For cotton cellulose, graphite furnace atomisation was required to detect all five elements, but for hay powder, the levels of copper and zinc were high enough to permit flame atomisation. It was found that dry-ashing led to the highest metal recoveries from the reference materials and was used thereafter in analysis of tree ring wood, bark and foliage. Results of dry ashing analyses for cotton cellulose and hay powder, plus certified data, are listed in Tables 2.5 and 2.6.

Table 2.5 Cotton cellulose V-9

	Experimental data			Certified data	
Element	N	X (µg/g)	s (µg/g)	Content (µg/g)	95% C.I. (µg/g)
Cd	8	0.003	0.001	0.002	0.001 - 0.006
Cu	8	0.57	0.04	0.59	0.47 - 0.94
Mn	8	0.13	0.03	0.15	0.12 - 0.21
Pb	8	0.21	0.02	0.25	0.22 - 0.33
Zn	8	0.52	0.06	0.55	0.21 - 7.2

Table 2.6 Hay powder V-10

	Experimental data			Certified data	
Element	N	X (μg/g)	s (μg/g)	Content (μg/g)	95% C.I. (μg/g)
Cd	6	0.02	0.01	0.03	0.02 - 0.05
Cu	6	8.7	0.3	9.4	8.8 - 9.7
Mn	6	0.43	0.03	0.47	0.32 - 0.52
Pb	6	1.6	0.1	1.6	0.8 - 1.9
Zn	6	19	2	24	21 - 27

It should be pointed out that although these SRMs resemble the actual samples measured in this study in chemical composition, their physical structures are not comparable. The SRMs have been homogenised by grinding to a fine powder, hence most of the physical destruction of the woody matrix has already taken place. Tree ring wood consists of an extremely resistant matrix of cellulose and lignin, and wet-ashing was found to be ineffective at breaking down this matrix.

An opportunity arose to obtain instrumental neutron activation analyses (INAA) on tree cores, so a 200 mg sample of cotton cellulose was also submitted. Results of the INAA analysis are given in Table 2.7. Comparisons were possible for only a few elements as many metals in cotton cellulose were below the detection limit of INAA. It can be seen that excellent agreement is obtained for Na, Cl, Br and Sc. Mn is poorer though still acceptable. INAA/FAAS comparisons for a whole tree core will be discussed in Chapter 5.

Table 2.7 Experimental data for INAA analysis of cotton cellulose V-9

	INAA	Certified data	
Element	X±s (μg/g)	Content (μg/g)	95% Confidence Limits
Na	54.1 (2.7)	56	49 - 64
Cl	600 (30)	603	490 - 640
Sc	0.0099 (0.0018)	0.009	0.007 - 0.010
Mn	0.200 (0.050)	0.15	0.12 - 0.21
Br	0.188 (0.088)	0.17	0.08 - 0.31

2.3 AAS / ASV COMPARISONS

A collector was placed at a suburban location and left for 6 months in order to collect sufficient material for more detailed study. The insoluble component was removed

from the container, dried and homogenised by grinding in an agate mortar and pestle. Prior to removing subsamples, the sample container was shaken thoroughly to ensure homogeneity. Ten accurately-weighed 0.1 g subsamples were digested with $HF/HClO_4$, and taken up in 2M HNO_3. Five samples were analysed by AAS (with flame atomisation for lead, zinc, copper and cadmium and graphite furnace atomisation for cadmium) and five were analysed by anodic stripping voltammetry. This technique is discussed in Section 7.3.2. The results are presented in Table 2.8

Table 2.8 Comparison of results obtained by AAS and ASV for dustfall.

	Pb		Zn		Cu		Cd	
Run	AAS	ASV	AAS	ASV	AAS	ASV	AAS	ASV
1	2290	2320	376	360	149	148	1.62	1.36
2	2180	2280	356	401	142	141	1.18	1.45
3	2340	2480	365	371	153	145	1.09	1.38
4	2240	2250	379	358	145	132	1.44	1.21
5	2300	2190	356	381	136	128	1.46	1.33
X*	2270	2300	366	374	145	139	1.35	1.35
(±s)	(62)	(109)	(11)	(18)	(6.5)	(9)	(0.16)	(0.088)

* X and s are the experimental means and standard deviations

The application of statistical comparison (Students t) tests to these sets of data showed that for all four metals, AAS and ASV analyses produced mean concentrations that are indistinguishable ($p>0.1$). Another feature of the data displayed in Table 2.8 is that the precision of the flame AAS analyses is generally better than 5% relative standard deviation (R.S.D.) with the precision of the ASV analyses slightly poorer at 5-7% R.S.D. The precision of the GFAAS cadmium analyses was poorer still, with an R.S.D. of 11.9%.

2.4 COMPARISONS WITH OTHER ANALYSTS

Two internal standards were used during this study for purposes of quality surveillance over time and also for comparisons with the results of other analysts.

2.4.1 Tai Tapu Silt Loam

This soil sample was collected and homogenised by N.D. Kim. It is a roadside topsoil sample from the outskirts of Christchurch. Its trace metal composition was found

to be typical of Canterbury Plains topsoils (discussed in chapter 4) although its proximity to a busy road has produced elevated levels of lead and, to a lesser extent, zinc.

Tai Tapu Silt Loam was included whenever a batch of soil samples was analysed. Results are presented in Table 2.9, together with the results obtained by N.Kim using the same extractant (4M HNO_3).

Table 2.9 Experimental data for Tai Tapu Silt Loam

Element	This study			Data of N. Kim		
	N	X(μg/g)	s(μg/g)	N	X(μg/g)	s(μg/g)
Cd	20	0.106	0.011	23	0.096	0.020
Cu	20	24.7	0.7	16	19.1	2.0
Pb	20	92.9	2.2	18	92.8	8.9
Zn	20	70.2	2.1	15	70.1	6.4

The application of the Students t comparison test to the data listed in Table 2.9 showed that the mean concentrations of zinc, cadmium and lead in Tai Tapu Silt Loam analysed by the author and by N. Kim were the same ($p<0.001$). In particular, the agreement between results for zinc and lead was extremely close. However, a highly significant difference was shown to exist between the mean concentrations obtained for copper, pointing to systematic errors in the measuring process of one or both of the analysts. A possible source of such errors could be the deterioration of standard solutions of copper.

2.4.2 Street dust RM-1

This material was collected and homogenised as part of a previous study (Fergusson and Simmonds, 1983). It is a roadside dust sample from beside Riccarton Road, which is a very busy main thoroughfare, and hence it contains very highly elevated levels of lead, and less highly elevated levels of zinc, copper and cadmium. Its composition is similar to urban dustfall, although soil will be a more important source for street dust.

This internal reference material was analysed many times throughout this study. The extractant used was 4M HNO_3, to enable comparison with the work of the above authors. Results from the present work, and from the study by Fergusson and

Simmonds, are displayed in Table 2.10. Fergusson (1987) also collated data for this internal standard obtained by several analysts over a period of 3 to 4 years. The results are also shown in Table 2.10.

Table 2.10 Experimental data for street dust RM-1

Element	This study			Fergusson and Simmonds (1983)			Fergusson (1987)		
	N	X(μg/g)	s(μg/g)	N	X(μg/g)	s(μg/g)	N	X(μg/g)	s(μg/g)
Cd	15	1.3	0.21	5	1.3	0.29	-	-	-
Cu	15	212	13	5	206	12	12	204	18
Mn	15	218	15	5	230	18	-	-	-
Pb	15	10 470	110	5	10 530	87	23	10 862	291
Zn	15	434	11	5	433	7	17	455	21

The application of Students t comparison tests to the data listed in Table 2.10 shows that there are no significant differences between the means obtained in this work, and Fergusson and Simmonds (1983) for the five elements measured. However, concentrations of lead and zinc reported by Fergusson (1987) are slightly higher than found by either this author or Fergusson and Simmonds. Mean concentrations of copper are the same.

2.5 CONCLUSION

In general, the agreement between the experimental data obtained during this study and the certified data for five standard reference materials was good, with acceptable values being produced in most cases. The results produced in this work tended to exhibit a slight negative bias towards incomplete recovery. This is probably because the main analytical technique used in this work was acid digestion followed by AAS determination, whereas the certified data also includes data from techniques such as neutron activation analysis and X-ray fluorescence which do not suffer from problems of incomplete recovery. The recovery of manganese from Soil-5 and sediment SD/N/1-2 was the lowest (≈83%). However, the proportion recovered was accurately characterised. Comparisons of results obtained for internal standards by other techniques and by other

analysts provide additional confidence that the measuring processes used in this study are producing acceptable and reliable data.

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Chapter 3

Deposition of airborne trace elements

3.1 INTRODUCTION

3.1.1 Deposition of metals from the atmosphere

Processes that remove particulate matter from the atmosphere fall into two categories : wet and dry deposition. Dry deposition is the removal of particles under dry weather conditions and consists of several processes. Particles may be transported to terrestrial surfaces by gravitational sedimentation (fallout), turbulent diffusion due to air currents, or by impaction against objects in the air stream. The relative importance of each process is controlled by several variables, especially particle size.

For large particles (>10 μm aerodynamic diameter) the overall dry deposition rate will be approximately equal to the rate of gravitational settling alone. With decreasing particle size, the dry deposition velocity does not decrease as rapidly as predicted by Stokes' Law because an additional contribution from turbulent diffusion becomes important. For very small particles, the deposition rate begins to rise again because of the increase in Brownian diffusivity with decreasing diameter (Davidson, 1980; Meszaros, 1981).

Wet deposition (or precipitation scavenging) is the removal of particulate matter by rain or snowfall. It is more efficient at particle removal than dry deposition because the falling speed of rain and snow greatly exceed dry deposition velocities (Meszaros, 1981). Two separate processes can be distinguished. Rainout refers to cloud formation on

aerosol condensation nuclei, and washout occurs when falling raindrops or snow crystals overtake and capture particles below the cloud base. Rainout is most efficient for particles less than 0.2 μm in diameter. These particles are characterised by their ability to become wetted by supersaturated water vapour and hence act as condensation nuclei (Noller et al., 1981).

The relative importance of wet and dry deposition has been widely investigated (Galloway et al., 1982; Jeffries and Snyder, 1981; Pierson et al., 1973; Lindberg and Harriss, 1982; Andren and Lindberg,1977; Lum et al., 1987; Galloway and Likens, 1978). Most of these studies reported the fraction deposited dry to be between 0.3 and 0.7. On theoretical grounds, Slinn (1977) calculated wet and dry deposition to be of roughly equal importance. The main influences on wet versus dry removal are rainfall amount and intensity, and the particle size distribution of the aerosol.

Collectors that are continuously open to the atmosphere collect both wet and dry deposition. Many such measurements have been made to determine total atmospheric loadings of metals to the environment (e.g. Lindberg and Harriss, 1981; Jeffries and Snyder, 1980; Sawicka-Kapusta, 1987). Concern over potential toxicity of heavy metals has led to measurements of solubility of metals in both wet and dry deposition to estimate their bioavailability (Gatz and Chu, 1986; Lum et al., 1987). Gatz and Chu concluded that dry deposition contains a lower, but still significant, soluble metal content than does wet deposition. Factors identified as being important in controlling the solubility of metal species are pH, and the presence of aluminosilicates and hydrous metal oxides, which are capable of adsorbing free metal ions. Also, solubilities of metal species are different for different metals, with zinc and cadmium species generally exhibiting greater solubility than copper or lead species.

3.1.2 Measurement of atmospheric deposition

Precipitation collectors may collect bulk (wet plus dry) fallout, or wet and dry fallout separately by means of a motor activated by rain or snowfall. Galloway and Likens (1978) review the performance of available collectors. To assess dry deposition only, Teflon plates are usually used (Elias et al., 1976; Huntzicker et al., 1975; Lindberg and Harriss, 1981).

Many authors have noted that the design of precipitation collectors have marked effects upon their collection efficiencies. In particular, aerodynamic blockage effects can accelerate and displace the airflow over the gauge opening. Sanderson et al. (1963) found that straight-sided jars collect around 40% of the dust gathered by aerodynamically-modified gauges. Another problem is that particles entering the gauges can be blown out again (Hall and Upton, 1988). This problem is most severe for gauges of approximately equal depth and diameter, because of internal circulation of air currents. To avoid blowout of particles, collectors should be either deep or shallow. Most conventional collectors are deep (usually around 40cm deep by 15cm diameter) but a recent novel suggestion is the use of inverted Frisbees as dust collectors (Hall and Waters, 1986).

Some authors have raised doubts about the relevance of fallout gauge measurements of deposition to the actual deposition received by natural terrestrial surfaces such as soil or grass. Davidson and Friedlander (1978) found that the nature of the receptor surface has an important effect on mechanisms of deposition, with sedimentation controlling deposition to flat surfaces whereas impaction controls deposition to vegetated surfaces. Several authors have designed collectors to simulate natural surfaces more closely. Schlesinger and Reiners (1974) found that compared with open jars, collectors containing artificial plastic conifer foliage recorded five times more deposition of lead. Much of this increase was due to a higher volume catchment but the authors pointed out that impaction must also be considered. Hirao and Patterson (1974) used artificial nylon sedge leaves to estimate fallout of lead aerosol but later (Elias et al., 1976) found that Teflon discs gave higher estimates.

An extension of the above ideas has been the use of actual vegetation surfaces to measure fallout. The use of non-rooted organisms such as mosses and lichens has received the most attention as these species receive all their nutrients from the atmosphere and avoid the complication of soil uptake. Bark is also known to be an effective collector of airborne metals and has been used as a qualitative indicator of aerial metal burdens (Tanaka and Ichikuni, 1982; Abergas et al., 1988). The deposition of metals onto trees, soil and peat will be investigated in the following chapters.

The most common application of biological monitoring is the use of moss-bags. This technique was pioneered by Goodman and Roberts (1971) and involves acidwashed samples of *Sphagnum* moss suspended in fine nylon mesh bags. Little and Martin (1974) indicated that a fairly strong positive correlation exists between deposit gauge estimates of fallout and results obtained with moss-bags. A more recent modification of the technique (Swaine et al., 1988; Godbeer et al., 1984) encloses the moss in flat mesh envelopes to provide a fallout estimate on an area basis.

A drawback of the moss-bag technique is that analytical blanks are high (e.g. Collins, 1988) for the measurement of low levels of metal deposition. In the previously-mentioned studies this problem was not important, as these measurements were carried out in the vicinity of metal smelters and coal-fired power stations.

The choice of technique to measure atmospheric metal deposition depends upon the aims of the study. If inputs to natural ecosystems are to be assessed, then the moss-bag technique is probably the most suitable. However, if deposition at remote sites is to be measured the moss-bag technique is prone to interference from high blank contributions and it is probably more suitable to use a conventional gauge, bearing in mind that this technique will provide a conservative estimate of the true amount of deposition. Another advantage of conventional collectors is that comparison with literature data is easier as the majority of studies to date have used this technique (Galloway et al., 1982).

3.1.3 Aims of this study

In this study, collection sites were established in the Canterbury Plains area to measure rates of atmospheric metal deposition at urban, rural and remote locations. The elevation of lead, zinc, copper and cadmium above background levels in the Christchurch environment is well-documented (Fergusson and Ryan, 1984) and by studying trends in atmospheric deposition with increasing distance from the city along several transect lines, it was hoped to gain an understanding of the atmospheric transport of these metals. During the initial stages of this work, street dust samples were collected along transect lines traversing the boundaries of the city. Analyses of these samples for lead, zinc, copper and manganese showed that an overall decrease in the concentrations of these

elements with increasing distance from the city centre was apparent, although fluctuations in this trend were quite large. For lead, the decrease was at least ten-fold over a distance of two kilometres.

Seasonal variations in rates of metal deposition are often high (Pierson et al., 1973; Swaine et al., 1988; Godbeer et al., 1984) because of seasonal changes in meteorological conditions. Two years of deposition data collected at each site enabled these seasonal changes to be studied, and related to available meteorological data.

Bulk precipitation collectors were used in this study. It is not possible to determine wet and dry contributions separately by this technique, since both have a soluble and insoluble component (Gatz and Chu, 1986). Preliminary analyses of Canterbury bulk deposition showed the insoluble fraction to account for ≈ 95% of lead, manganese and cadmium deposition, ≈90% of copper and ≈75% of zinc. Trends in metal solubility in relation to rainfall amount and pH were studied for a years' data but only the insoluble fraction was measured for the remainder of the sampling programme.

3.2 EXPERIMENTAL

3.2.1 Sampling sites

The locations of the collectors, in relation to the geographical features of Canterbury, are shown in Figures 3.1 and 3.2. Details of the sites are listed in Table 3.1.

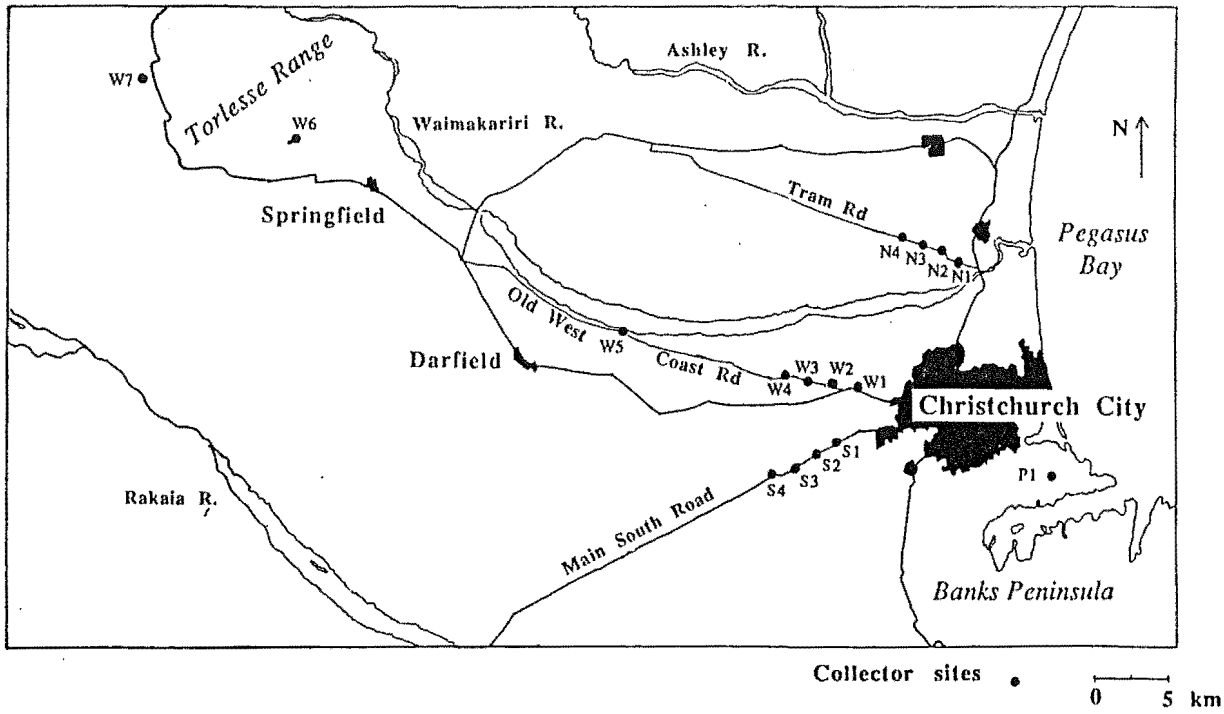

Figure 3.1 Canterbury Plains, N.Z., showing location of dustfall collectors

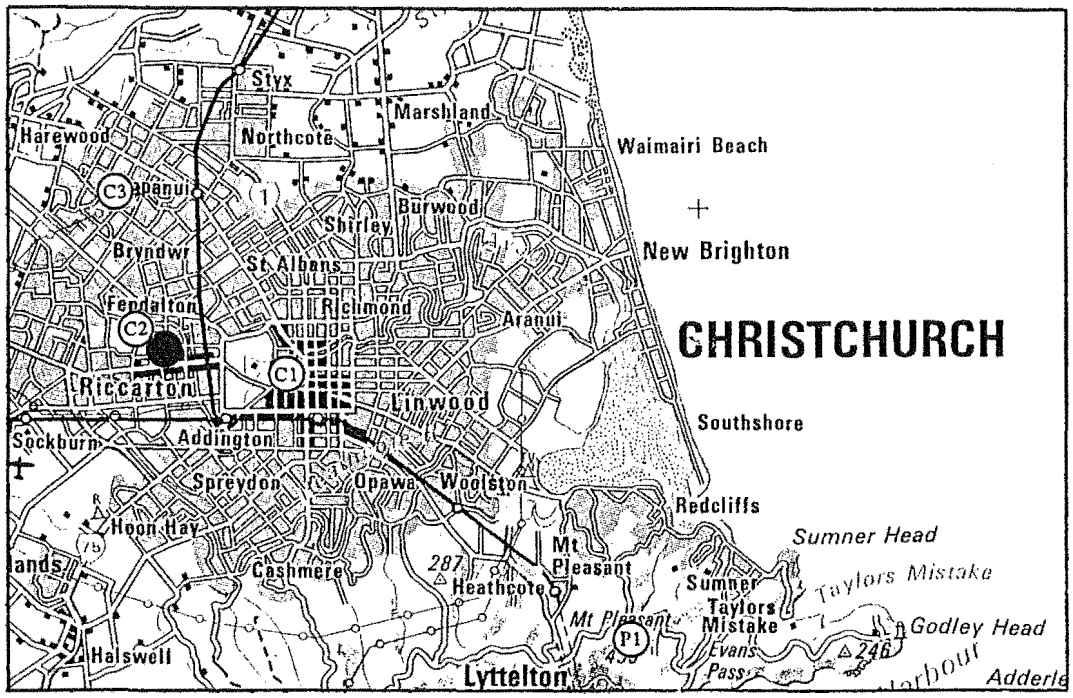

Figure 3.2 Christchurch city, N.Z., showing location of dustfall collectors (open symbols) and Riccarton Bush (closed symbol)

Table 3.1 Details of collection sites

Site	Map reference*	Distance from Chch(km)	Direction from Chch	Distance(m) from road	Comments
N1	479 756	14.0	NW	50	Car workshop nearby
N2	477 757	16.0	NW	100	
N3	476 758	16.5	NW	20	
N4	474 758	17.5	NW	40	
W1	469 444	11.5	W	150	
W2	467 745	14.0	W	200	Gravel-crushing works 200 m to south
W3	464 744	16.2	W	150	
W4	463 745	18.0	W	500	
W5	445 751	36.8	W	50	
W6	415 767	69.0	W	3000	Lake visited for shooting at times
W7	406 775	80.5	W	500	Geographically separated from Canterbury plains by Torlesse Range
S1	466 741	14.3	SW	1500	Located in hospital grounds
S2	466 738	15.5	SW	100	
S3	464 736	17.5	SW	750	
S4	462 735	19.5	SW	200	Old farm machinery nearby
P1	487 731	9.0	SE	750	Very windy, exposed site
C1	480 742	0.5	-	20	Inner city site; very high traffic density
C2	477 743	4.0	-	40	Quiet residential (Riccarton)
C3	476 746	6.4	-	20	Quiet residential (Bishopdale)

3.2.2 Design and siting of the collectors

The basic design of the American standard collector (ASTM, 1983) was adopted in preference to the more complex British gauge (BS 1747, 1969). The collectors were constructed of PVC pipe (150 mm internal diameter x 400 mm depth) with a PVC cap fitted onto the base. The collectors were supported by 1.5 m high aluminium tripods which could be pushed firmly into the ground. An aluminium bird ring was attached above the container to discourage birds from settling on the rim. The collector and tripod are shown in Plate 3.1.

Plate 3.1 Dustfall collector, tripod and bird ring

Some problems were experienced with tripods collapsing in strong winds and where possible, an alternative system of wiring the collectors onto fence posts was adopted. It is very important to ensure that the top of the collectors are horizontal. Hall and Upton (1988) found that tilting a collector can have considerable effects upon its collection efficiency.

Care was also taken to locate collectors in open spaces well away from any obstacles such as buildings or shelter belts that may cause aerodynamic blockage of the airflow. The British Standards Association recommend that the distance to any obstacle be at least twice the height of the object above the collector. Buildings or trees may also add a component of contamination to the dustfall. Sites free from human and stock interference are desirable, but in practice, the collectors had to placed at the convenience of the landowner.

3.2.3 Cleaning of the collectors

Initially, the containers were soaked in hot, soapy water overnight and rinsed well with tap water then single-distilled water. Containers were then soaked in 2 mol l^{-1} HNO_3 (AR grade) for a week then rinsed thoroughly with double-distilled water.

While not in use, the containers were soaked in 1 mol l^{-1} HNO_3 (AR grade) for at least 2 days then rinsed thoroughly with double-distilled water. The rinsing water was tested to ensure that all traces of wash acid had been removed, as insoluble and soluble deposition was measured separately and residual acidity in the containers may affect the speciation and solubility. The containers were drained thoroughly and stored covered with several layers of plastic film.

The possibility of leaching of metals out of the PVC was investigated by allowing a volume of double-distilled water (adjusted to pH values of 3.0, 4.0, 5.0 and 6.0 with Aristar HNO_3) to contact the PVC for times of 0,1,2,3 and 6 months. These conditions were chosen to be relevant to this study. It was found that even at pH 3.0, six months of leaching did not result in detectable (by graphite furnace AAS) concentrations of lead, zinc, copper, manganese or cadmium. Hence leaching from the containers was not considered to be a problem.

3.2.4 Length of sampling period

In order to collect enough material for analysis, it was found to be necessary to leave collectors in urban locations for 1 month, in rural locations for 3 months and in remote locations for 6 months.

3.2.5 Field handling of collectors

The collectors were transported to the sites protected with a covering of plastic film, which was removed once the collector was installed on the tripod. At the end of the sampling period, the collectors were covered with plastic film and sealed in polythene bags for transport back to the laboratory. The apparatus was always handled wearing disposable plastic gloves. Recovery of the contents was carried out inside the Clean Room.

3.2.6 Recovery of deposition from collectors

a) Soluble component The volume of rainwater in each collector was recorded, and 250 ml retained for analysis. If there was less than 250 ml, the entire amount was retained. Often the container was dry (either because of no rainfall or evaporation). In these cases, 250 ml of double distilled water adjusted to pH 5.8 (the measured average of the rainwater) was added to each container to estimate the soluble component and allowed to equilibrate overnight. The pH of each sample was measured with a glass-calomel electrode couple.

Storage of water samples is an important aspect of analysis. Florence (1986) and Gatz and Chu(1986) have recommended that natural water samples do not be acidified during storage, because the speciation of natural waters is dominated by stable soluble metal-organic complexes which will not adsorb to container walls. Acidification of samples may alter speciation, producing the free metal ion. It is preferable to store natural water samples at 4°C until analysis, without acidification.

b) Insoluble component The insoluble material was washed out of the collectors into acid-washed glass centrifuge tubes. Leaves and twigs were removed with plastic tweezers. The solutions were centrifuged at 3000 r.p.m. for 30 minutes, and the supernatant decanted off. The supernatant washing water was measured for redissolved lead, zinc, copper, manganese and cadmium but none were detected.

3.2.7 Analytical Procedures

a) Soluble component The water samples were preconcentrated for analysis by freeze-drying. Several techniques such as solvent extraction, nonboiling evaporation and ion-exchange are often used for analysis of clean water and snow samples. However, freeze-drying was the method of choice in this study as the apparatus was readily available and problems of airborne contamination are avoided as the system is closed to the atmosphere.

Samples were removed from cold storage and 250 ml of each placed in acid-washed 500 ml Pyrex round-bottomed flasks. Each flask was sealed with plastic film and frozen solid at -15°C. The flasks were attached to the freeze-drier and the vacuum applied. This step had to be carried out quickly before remelting occurred. Complete

sublimation of the ice took around 2-3 days. After this, the flasks were removed from the freeze-drier and sealed with plastic film. The next steps were performed in the Clean Room. To dissolve the residue, 25.00 ml Aristar grade 2M HNO_3 was added by pipette, and the solution warmed under an infrared heat lamp until the residue had dissolved. To avoid contact with the vacuum grease on the neck of the flasks, a 20 ml aliquot was removed for analysis by pipette. Blanks were run simultaneously with the samples for the freeze-drying step.

The solutions were analysed by graphite furnace AAS for lead, copper and cadmium at 217.0 nm, 324.8 nm and 228.8 nm. Zinc and manganese were easily detectable using flame AAS at wavelengths of 213.9 nm and 279.5 nm. The use of H_3PO_4 as a matrix modifier was found to be unnecessary. From the concentration of metal in the freeze-dried solution, the mass of metal in the original volume of rainwater was calculated.

b) Insoluble component The insoluble material was transferred from the centrifuge into acid-washed platinum crucibles. The samples were dried at 80°C in a clean oven, then ashed at 400°C to constant weight. The temperature was kept below 430°C to avoid the reported loss of volatile species above this temperature (Webber, 1972).

A total dissolution of the insoluble material was achieved using the strong acids HF and $HClO_4$. To each crucible was added 6 ml 40% HF (grade) and 1 ml $HClO_4$ (Aristar grade). The crucibles were placed in a sand bath at 180°C and the mixed acids fumed off. A perspex hood shielding the crucibles from airborne contamination was found to be necessary for this step. The digestion was repeated using 3 ml HF and 0.5 ml $HClO_4$ until a white residue was obtained. The residue was taken up in 10 ml 2M Aristar grade HNO_3 and stored at 4°C until analysis. Cadmium was determined by graphite furnace AAS whereas lead, zinc, copper and manganese were readily detectable by flame AAS.

3.3 RESULTS AND DISCUSSION

3.3.1 Spatial variations in insoluble metal deposition rates over Canterbury

For each site, an average deposition rate over the whole sampling period (based on data listed in Appendix 3.1) is listed in Table 3.2. The geographical location of each site is shown in Figure 3.1.

Table 3.2 Average deposition of metals at collection sites

Site	Deposition Rate ($\mu g/m^2/day$)* Pb	Zn	Cu	Mn	Cd
W1	78 (26)	19 (42)	5.4 (35)	24 (29)	0.44 (30)
W2	72 (26)	22 (12)	4.1 (49)	23 (30)	0.46 (39)
W3	66 (32)	21 (55)	3.7 (84)	25 (44)	0.43 (51)
W4	55 (27)	16 (56)	2.5 (92)	20 (55)	0.42 (57)
W5	20 (30)	8.8 (42)	6.2 (53)	26 (85)	0.015 (53)
W6[a]	87(18)	7.0(43)	2.7(41)	13(8)	0.024(13)
W7	1.8 (11)	1.8 (11)	0.83 (52)	31 (35)	0.0058 (21)
S1	90 (42)	24 (46)	6.5 (66)	21 (67)	0.62 (42)
S2[a]	79	27	5.4	24	0.51
S3	73 (25)	22 (55)	4.3 (53)	16 (56)	0.44 (57)
S4	69 (26)	15 (33)	4.6 (48)	19 (32)	0.42 (57)
N1	40 (28)	12 (42)	4.2 (62)	20 (45)	0.34 (38)
N2	45 (38)	23 (9)	4.2 (48)	16(19)	0.27 (33)
N3[b]	56	22	1.0	22	0.29
N4	44 (45)	13 (54)	2.8 (93)	20 (25)	0.31 (29)
P1	31 (19)	16 (63)	4.7 (72)	31 (16)	0.24 (50)
C1	343 (39)	227 (33)	21 (29)	23 (22)	5.9 (53)
C2	160 (56)	100 (38)	11.6 (29)	22 (59)	4.3 (47)
C3	155 (31)	96 (61)	9.2 (22)	20 (30)	3.4 (32)

* Deposition rates are the average of all the measurements over the 2-year sampling period unless otherwise indicated. The number in brackets is the relative standard deviation (% R.S.D.) of the individual measurements, where R.S.D. = (standard deviation/mean) x 100%.
a 2 measurements
b 1 measurement

The data in Table 3.2 indicate that levels of deposition vary greatly with location. Spatial trends will be analysed and discussed in detail below.

a) Interelement correlations Interelement correlations based on Table 3.2 are listed in Table 3.3. The data in Table 3.3 show that lead, zinc and copper are highly significantly correlated with each other ($p<0.001$). These metals show very significant

correlations ($p<0.01$) with cadmium. Manganese shows no correlation with the other metals. These correlations suggest that lead, zinc, copper and cadmium may originate from a common composite source, with manganese levels being controlled by a different source. The high concentration values of lead, zinc, copper and cadmium in city deposition tend to weight correlation coefficients, and may obscure trends within the rural and remote sets of data.

Correlation coefficients were recalculated omitting the data from the city sites. It was found that correlations were weaker in all cases, with the only highly significant ($p<0.001$) correlation occurring between zinc and cadmium. These elements are geochemically associated and are often observed to occur together. Correlations with copper and lead were either significant ($p<0.02$) or very significant ($p<0.01$).

Table 3.3 Interelement correlations for deposition data (N=19 pairs*)

	Pb	Zn	Cu	Mn	Cd
Pb	-	0.933	0.861	0.004	0.626
Zn		-	0.901	0.005	0.697
Cu			-	0.038	0.664
Mn				-	0.002
Cd					-

* For N=19, $r \geq 0.6652$ are highly significant ($p<0.001$)
$r \geq 0.5487$ are very significant ($p<0.01$)

It should be noted at this point that significance levels relate to normally-distributed data sets. Because environmental concentrations of metals are in fact often log-normally distributed, many of the significance levels quoted in this study should be taken as a guide only. However, when the data listed in Table 3.2 was log-transformed, it was found that interelement correlations were very similar to those listed in Table 3.3.

b) Relationship between levels of deposition and distance from the city The average deposition of each metal, with respect to distance from the centre of Christchurch, is shown graphically in Figures 3.3 to 3.7.

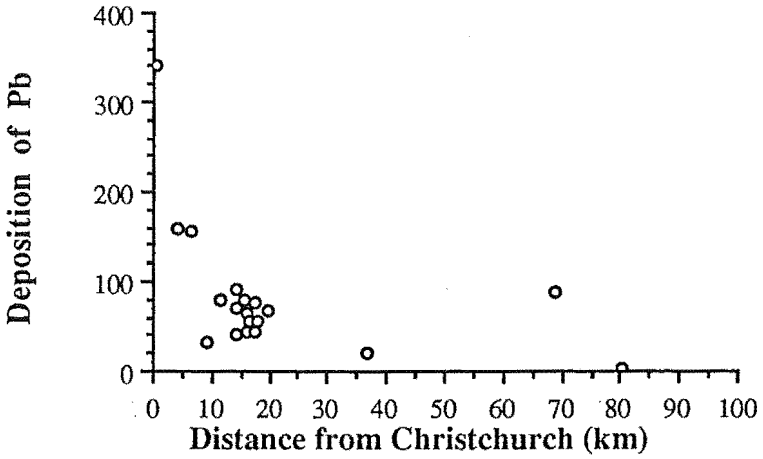

Figure 3.3 Deposition of Pb (μg/m^2/day) vs distance from Christchurch

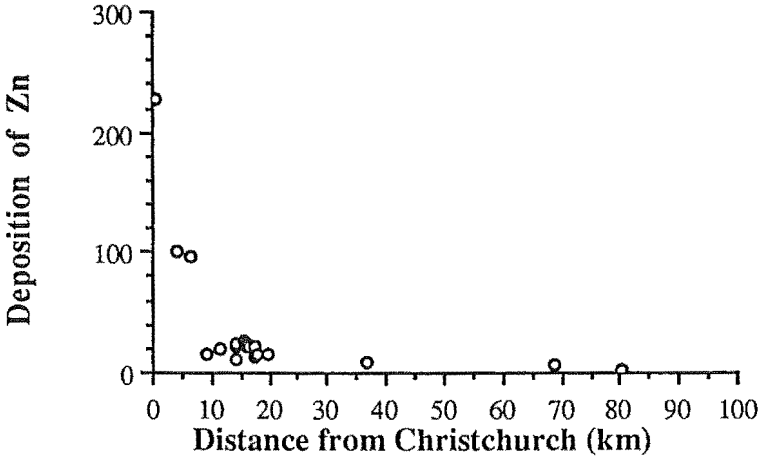

Figure 3.4 Deposition of Zn (μg/m^2/day) vs distance from Christchurch

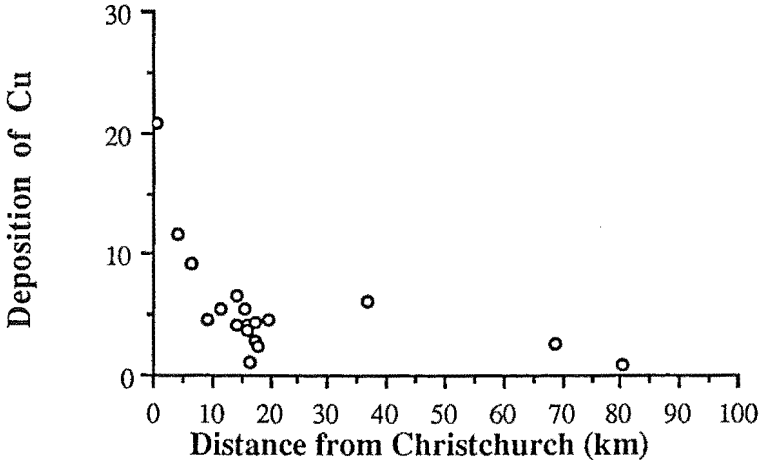

Figure 3.5 Deposition of Cu (μg/m^2/day) vs distance from Christchurch

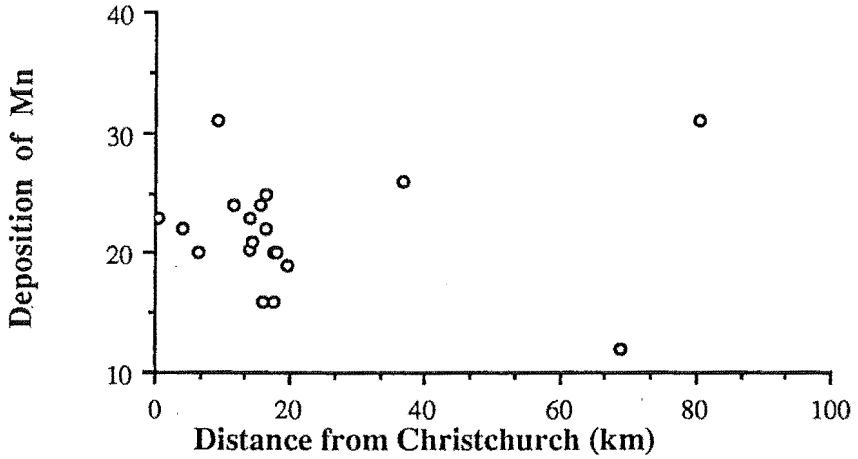

Figure 3.6 Deposition of Mn (μg/m^2/day) vs distance from Christchurch

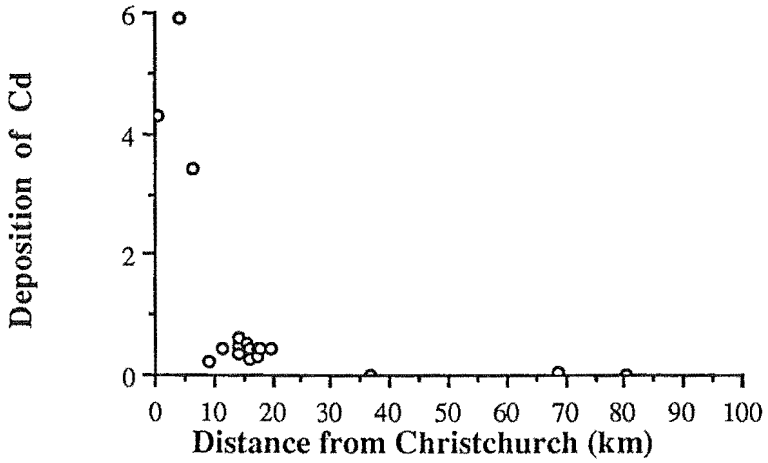

Figure 3.7 Deposition of Cd (μg/m^2/day) vs distance from Christchurch

From the information displayed in Figures 3.3 to 3.7, it appears that the deposition of lead, zinc, copper and cadmium decreases with increasing distance from Christchurch in an approximately exponential manner, whereas manganese deposition shows no particular trends with distance. If the deposition rates are plotted on a logarithmic scale, a straight-line relationship becomes apparent. Lead deposition is shown as an example in Figure 3.8.

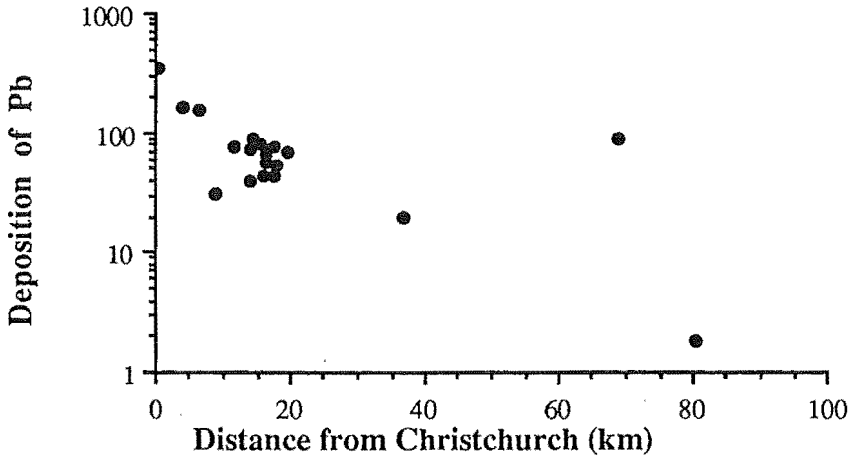

Figure 3.8 Deposition of Pb (μg/m²/day) plotted on a log scale, versus distance from Christchurch

By use of a curve-fitting programme, curves of the form $y = a.e^{-kx}$ were fitted to each set of data and r (goodness of fit) values computed for each. Results are listed in Table 3.4.

Table 3.4 Goodness for fit (r) values of exponential decay curves to deposition versus distance data (N=19)

Element	r	Significance*
Pb	0.701	p<0.001
Zn	0.817	p<0.001
Cu	0.623	p<0.01
Mn	0.004	p>0.1
Cd	0.877	p<0.001

* p<0.001 highly significant
p<0.01 very significant
p>0.1 not significant

Thus, lead, zinc and cadmium deposition data show the closest degree of fit to an exponential decay curve, followed by copper. The manganese data are not well described by an exponential curve. An exception to the decay pattern is the high level of lead deposition recorded at site W6. If this point is disregarded, a value of r=0.924 for a fitted exponential curve is obtained. The reason for the anomalous value is not clear. One possibility is contamination from human interference. The location is known to be visited for hunting and fishing.

Many authors have reported a curvilinear decrease away from a source in atmospheric concentrations of metals as well as levels in surface vegetation and soils

(Chamberlain et al., 1979; Ward et al., 1975; Little and Wiffen, 1978; Davies, 1980; Motto et al., 1970; Chow, 1973; Lagerwerff and Specht, 1970). Frequently the decrease is well-described by an exponential type of decay curve.

c) Relationship between levels of lead deposition and distance from roads The pattern of lead deposition over the Canterbury Plains could be confused by the presence of numerous major and minor roads, which act as line sources of lead emissions (Davies, 1980). The elevation of lead levels in roadside soils, air and vegetation is well-documented (e.g. Davies, 1980; Chow, 1973) and depends on traffic density, distance from the road, and the direction of the prevailing wind.

It was difficult to study the effect of roads on rural lead deposition in isolation from the effect of increasing distance from the city. An attempt was made by calculating linear regressions for lead deposition at rural collectors versus distance of each collector from the nearest road. Each transect line was considered separately, as the traffic volumes along each were different. It was found that a "just significant" ($p<0.05$) correlation existed for the Old West Coast Road transect (see Figure 3.1) but no correlations were found for the other lines. Hence, the effect of nearby roads on lead deposition at rural collection sites was unimportant compared with the effect of distance from the city.

d) Deposition rates with respect to orientation of transect lines The data presented in Figure 3.3. is shown replotted in Figure 3.9, using different symbols for each transect line. It can be seen that systematic differences exist between the transect lines, with deposition at a given distance being higher along the SW transect, followed by the W then the NW transect lines. This is consistent with wind data obtained from the Christchurch Meteorological Office (pers. comm.) indicating that the prevailing wind direction in Christchurch is north-easterly. Hence this pattern compares with what is expected from point or area sources of contamination (Davies, 1980; Little and Martin, 1974), which is a broadly elliptical pattern of dispersal with the major axis extending in the direction of the prevailing wind.

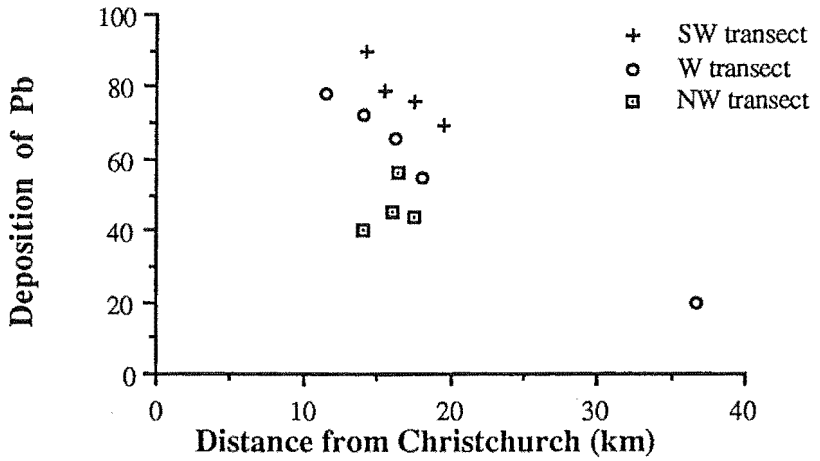

Figure 3.9 Deposition of Pb ($\mu g/m^2/day$) by transect line

Another feature of Figure 3.9 is that along the W and SW transect lines, rates of deposition decrease progressively with increasing distance. However, the NW transect does not show this pattern. This may be partly because the sites lie upwind from the city, and also because the line does not radiate from the city but more nearly lies parallel to it (Figure 3.1).

3.3.2 Comparisons of deposition rates in Canterbury with literature data

The data presented in Table 3.2 is summarised in Table 3.5, together with data from several comprehensive reviews of global deposition data (Galloway et al., 1982; Nriagu and Davidson, 1979; Nriagu, 1978, 1980a. 1980b).

Table 3.5 Comparison between Canterbury deposition data and literature values

		deposition ($\mu g/m^2/day$) This study	Galloway	Nriagu
Pb	Urban	150-350	50-500	>60
	Rural	20-90	5-80	10-60
	Remote	1.8	0.003-2.5	<10
Zn	Urban	100-200	100-4000	>150
	Rural	10-30	<150	50-150
	Remote	1.8	0.003-6.8	<60
Cu	Urban	10-20	40-160	100-550
	Rural	2-6	5-60	1-100
	Remote	0.83	0.003-0.5	0.2-1.0
Mn	Urban	20-25	<250	-
	Rural	20-30	3-130	-
	Remote	30	1.7	-
Cd	Urban	4-6	2-70	5-20
	Rural	0.3-0.6	0.3-2.4	0.2-2.7
	Remote	0.0058	0.0006-0.014	-

To summarise Table 3.5, rates of deposition of zinc, copper and cadmium are generally lower in Canterbury than data for other countries reported in the literature. Lead deposition rates, however, are comparable to or higher than their overseas counterparts. The lead flux in the most remote collection site in this study was 1.8 $\mu g/m^2/day$. This is similar to a background flux of 5 $\mu g/m^2/day$ reported by Collins (1988), for a valley near Dunedin. However, reservations have already been expressed about the methodology used in this study, as a large procedural blank of 66 $\mu g/m^2/day$ was reported. Specific lead fluxes for other remote areas are 10 $\mu g/m^2/day$ to remote Northern Hemisphere continental locations (Settle and Patterson, 1980); 3 $\mu g/m^2/day$ to Northern Hemisphere oceans (Settle and Patterson, 1982); 0.3 $\mu g/m^2/day$ in the Southern Ocean in the vicinity of New Zealand (Steiner and Clarkson, 1985); and 0.002 $\mu g/m^2/day$ to the Antarctic ice cap (Boutron and Patterson, 1983). Settle and Patterson (1980) noted that in the Southern Hemisphere, lead pollution effects in remote, nondomesticated areas are estimated to be about one-tenth of those in the Northern Hemisphere, since about 90% of the anthropogenic lead aerosols are emitted in the Northern Hemisphere and

interhemispheric mixing is inefficient. The value of 1.8 $\mu g/m^2$/day obtained for the most remote location in this study is reasonably consistent with this argument.

Manganese deposition rates show very little spatial variation in Canterbury and are low compared with reported data. This is probably a reflection of the soil origins of much airborne manganese, as manganese levels in Canterbury soils are generally lower (300-400 $\mu g/g$) than reported ranges of manganese concentrations in overseas soils (e.g. 500-1000 $\mu g/g$, Adriano, 1986).

The difference between lead and the other pollutant metals is worthy of further comment. It is well-known that ambient concentrations of lead in the Christchurch atmosphere are greater than in many overseas cities (Simmonds et al., 1983). Contributing factors identified are the high lead content of New Zealand petrol (0.84 g l^{-1} until July 1986) and the relatively calm conditions common in winter. Another indicator of atmospheric levels of metals is urban street dust. Fergusson and Ryan (1984) found that lead concentrations in Christchurch street dust could exceed concentrations in dust from London, New York, Halifax or Kingston. Levels of zinc, copper and cadmium were generally lower in Christchurch dust. Calculation of enrichment factors relative to crustal abundance showed lead to be enriched around ten times more than the other metals. Thus, it seems likely that high rates of lead deposition in urban and rural locations in Canterbury may be related to the high ambient concentrations of lead in Christchurch, which have been attributed to lead additives in petrol (Simmonds et al., 1983; Day, 1976).

In July 1986, the lead content of New Zealand 96 Octane Premium Grade Petrol was reduced from 0.84 to 0.45 g l^{-1}, and a grade of unleaded petrol became available in January 1987 (Department of Health, 1987). A corresponding reduction in lead concentrations in Auckland urban air was reported in the above study. On a quantitative basis, Page et al (1988) reported a 52-61% reduction in air lead following a 63% reduction in petrol lead in Wales, and similarly Jost and Sartorius (1979) reported a 60% reduction following a 63% reduction in German petrol.

Hence, a reduction in lead deposition rates after July 1986 might be expected in this study, although any reduction will be superimposed upon marked seasonal variations

in deposition fluxes (Section 3.3.4). Despite the limited number of data points before July 1986, it was possible to perform a simple statistical comparison of deposition data before and after July 1986 at urban and rural sites, using a form of Students' t - test. Results of the comparison tests indicate that significant differences in deposition rates existed at the following sites : C1 ($p<0.025$), C3 ($p<0.10$), S1 ($p<0.01$), S3 ($p<0.10$), S4 ($p<0.025$) and W2 ($p<0.05$). At the remainder of the sites, no such difference was demonstrated.

To provide a crude estimate of the size of the reduction, the mean deposition rates before and after July 1986 were compared for the above-mentioned sites. There was found to be an average reduction of $(35 \pm 9)\%$. However, it is not known what effect variations in meteorological conditions from one year to the next may have, and more data prior to the date of the reduction of lead in petrol would be necessary to evaluate these variations.

The seasonal data is displayed graphically in Figure 3.10, and in general, the winter deposition maximum appears lower in 1987 than in 1986.

3.3.3 Sources of metals in deposition

Methods that have been used to deduce sources of components of deposition include calculation of enrichment factors, correlation coefficients, factor analyses and chemical element balances (references cited in Fergusson and Ryan, 1984).

Interelement correlation coefficients were calculated and discussed in Section 3.3.1. These showed that levels of lead, zinc, copper and cadmium tend to follow each other and hence a similar composite source for these elements is indicated.

Enrichment factors (EFs) relative to a reference material (usually soil or crustally-derived dust) have been used to indicate the origins of atmospheric particulates (Galloway et al., 1982; Wiersma and Davidson, 1986). An enrichment factor of around one indicates that the element is not enriched in the atmosphere and that the reference material is the main source. Enrichment factors are usually calculated for airborne concentrations of metals ($\mu g/m^3$) or as $\mu g/g$ of total insoluble mass. To enable enrichment factors to be calculated, deposition data (in units of $\mu g/m^2/day$)were recalculated as $\mu g/g$, using the total insoluble mass recorded for each collector. Enrichment factors relative to soil were

calculated using the formula $EF_X = X_{dust}/Mn_{dust} \times Mn_{soil}/X_{soil}$. Results from remote (W7), rural (W4) and urban (C1) sites are presented in Table 3.6

Table 3.6 Enrichment factors for dustfall relative to soil

Element	Urban (C1)	Rural (W4)	Remote (W7)
Pb	1060	118	3.9
Zn	55	5.8	1.2
Cu	56	8.9	3.3
Mn	1.0	1.0	1.0
Cd	111	64	1.6

It is evident from the data in Table 3.6 that non-soil sources are contributing lead, zinc, copper and cadmium to urban dustfall, with the enrichment being largest for lead and cadmium. The enrichment of these metals in remote dustfall is close to unity, suggesting that soil is the main source of these elements in remote dustfall. At the rural site, lead and cadmium are still enriched considerably over soil concentrations, suggesting that this site is influenced by urban sources of these metals. However, copper and zinc enrichments suggest that soil may be a more important source of these metals in rural deposition.

If it assumed that all the manganese in dustfall is soil-derived, then the following percentages for the relative contribution of soil to dustfall can be calculated from the ratio Mn_{dust}/Mn_{soil}. Percentages of 60% for urban dustfall, 91% for rural dustfall and 104% for remote dustfall were obtained. The figure of 60% for urban dustfall is lower than a value of 75-90% for Christchurch street dust, estimated by Fergusson and Ryan (1984). However, a higher contribution of soil to street dust than to airborne particulate matter is not surprising.

Another comment arising from the data in Table 3.6 is that enrichments of lead, zinc, copper and cadmium in New Zealand remote dustfall are very low compared to EF values for these metals in other remote areas of the world. In fact, these metals, plus several others, are termed anomalously enriched elements (Wiersma and Davidson, 1986), with geometric mean crustal enrichments ranging from 25 (for copper) to 1100 (for cadmium). High enrichments have been observed in Antarctica, and there has been

much debate over whether these high enrichments are natural or anthropogenic in origin (Boutron and Delmas, 1980; Boutron, 1979; Ng and Patterson, 1983; Boutron, 1986). The most recent evidence, based on analyses of historical trends of deposition recorded in ice cores, suggests that observed enrichments arise from natural processes, especially vulcanism and biogenic emissions. It appears that in remote sites in New Zealand, natural enrichment processes such as vulcanism do not contribute significantly to the aerosol, and that observed levels of lead, zinc, copper and cadmium are mostly accounted for by soil-derived particles.

3.3.4 Seasonal variations in deposition rates

The data listed in Appendix 3.1 has been plotted in a three-dimensional form, thus enabling temporal trends in deposition to be viewed simultaneously for all sites. These plots are shown in Figures 3.10 to 3.14.

The spatial trends are complex, but there are similarities between lead, zinc, copper and cadmium patterns. The most obvious trend is that depositional data appears to be seasonal in nature, with winter maxima at most sites. Deposition of manganese appears more randomly distributed, with perhaps some similarity to the other metals.

The importance of meteorological factors in controlling the dispersal and transport of atmospheric constituents is well-known (e.g. Noller et al., 1981; Sturman, 1985; Witz and Moore, 1981; Pierson et al, 1973). Seasonal changes in meteorological conditions in Christchurch are plotted in Figure 3.15.

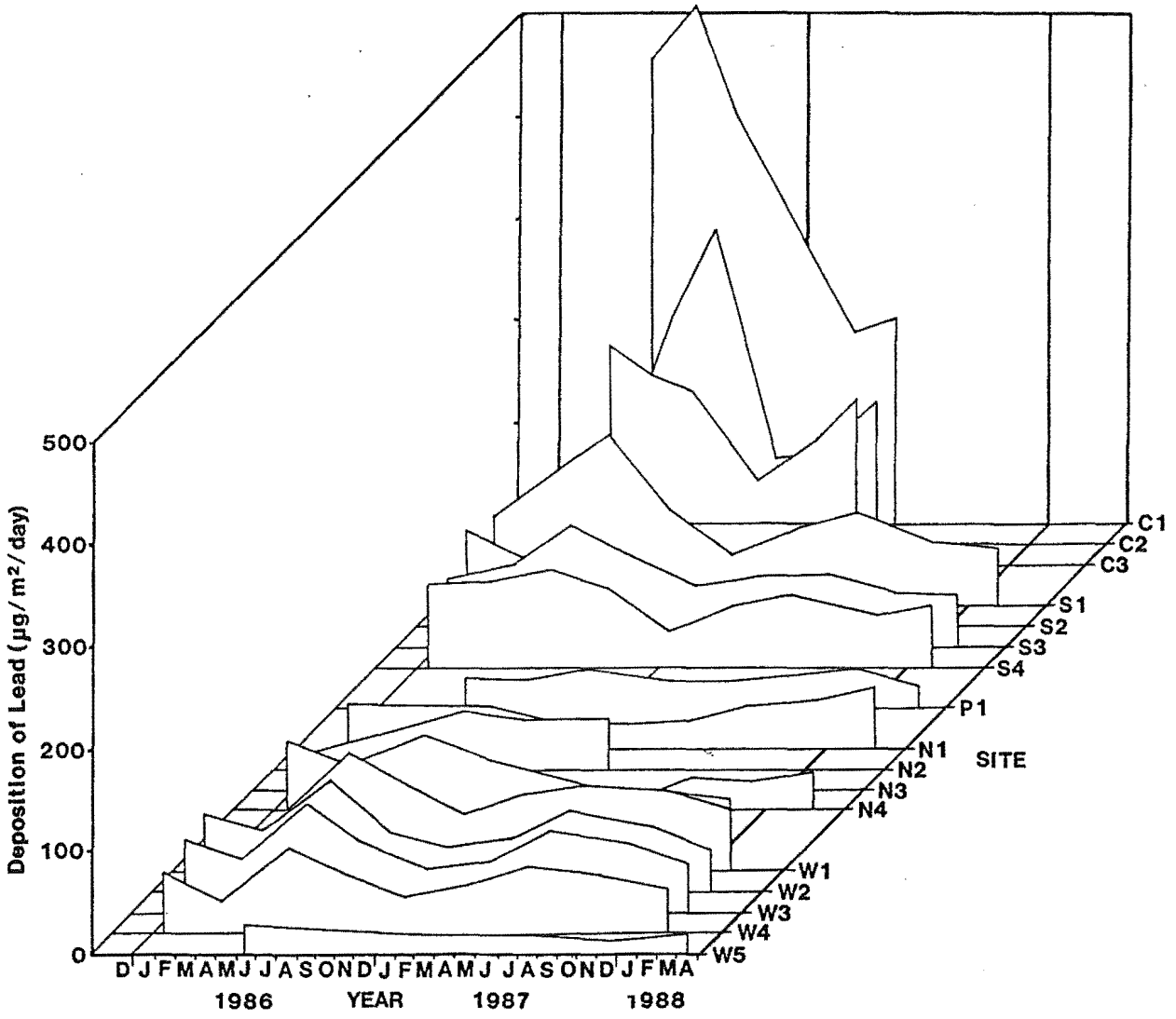

Figure 3.10 Seasonal variations in Pb deposition

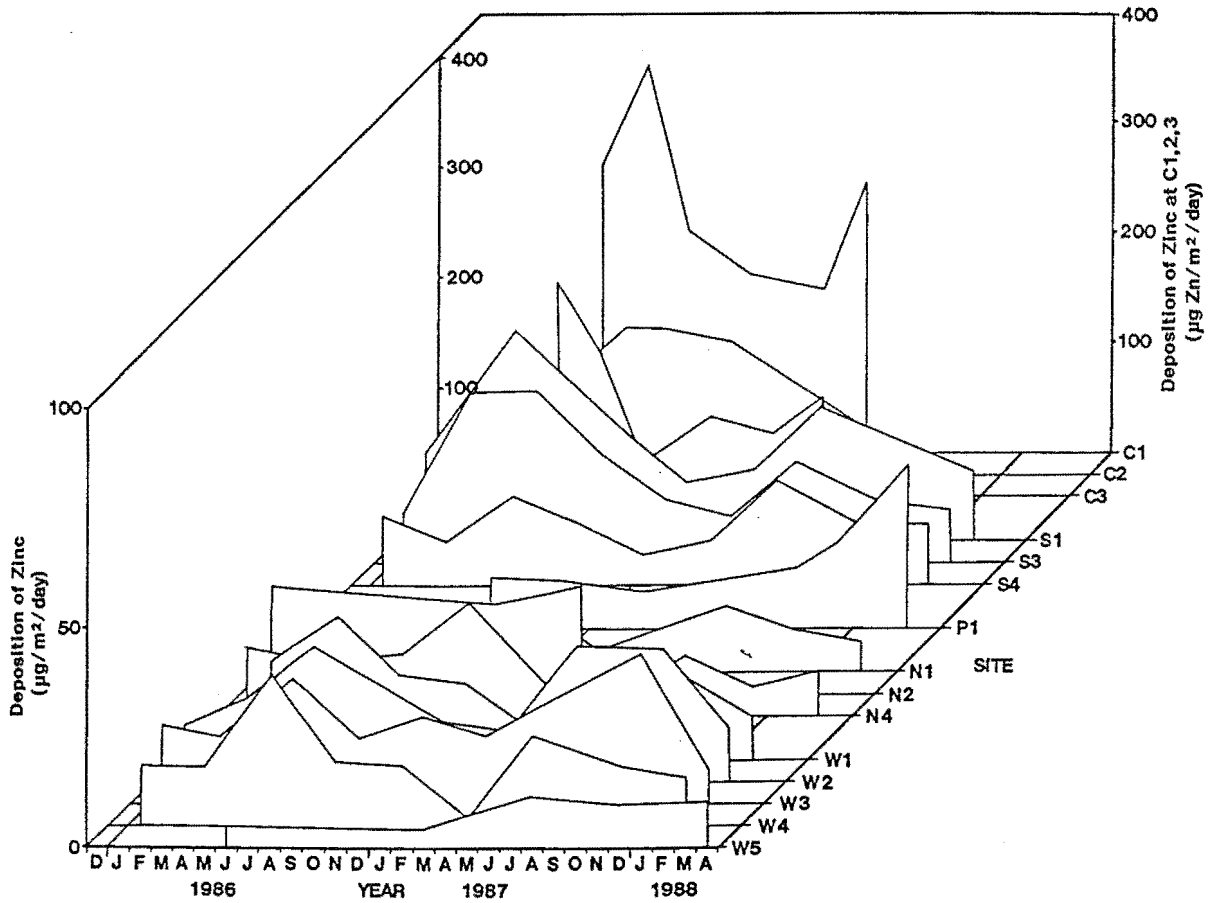

Figure 3.11 Seasonal variations in Zn deposition

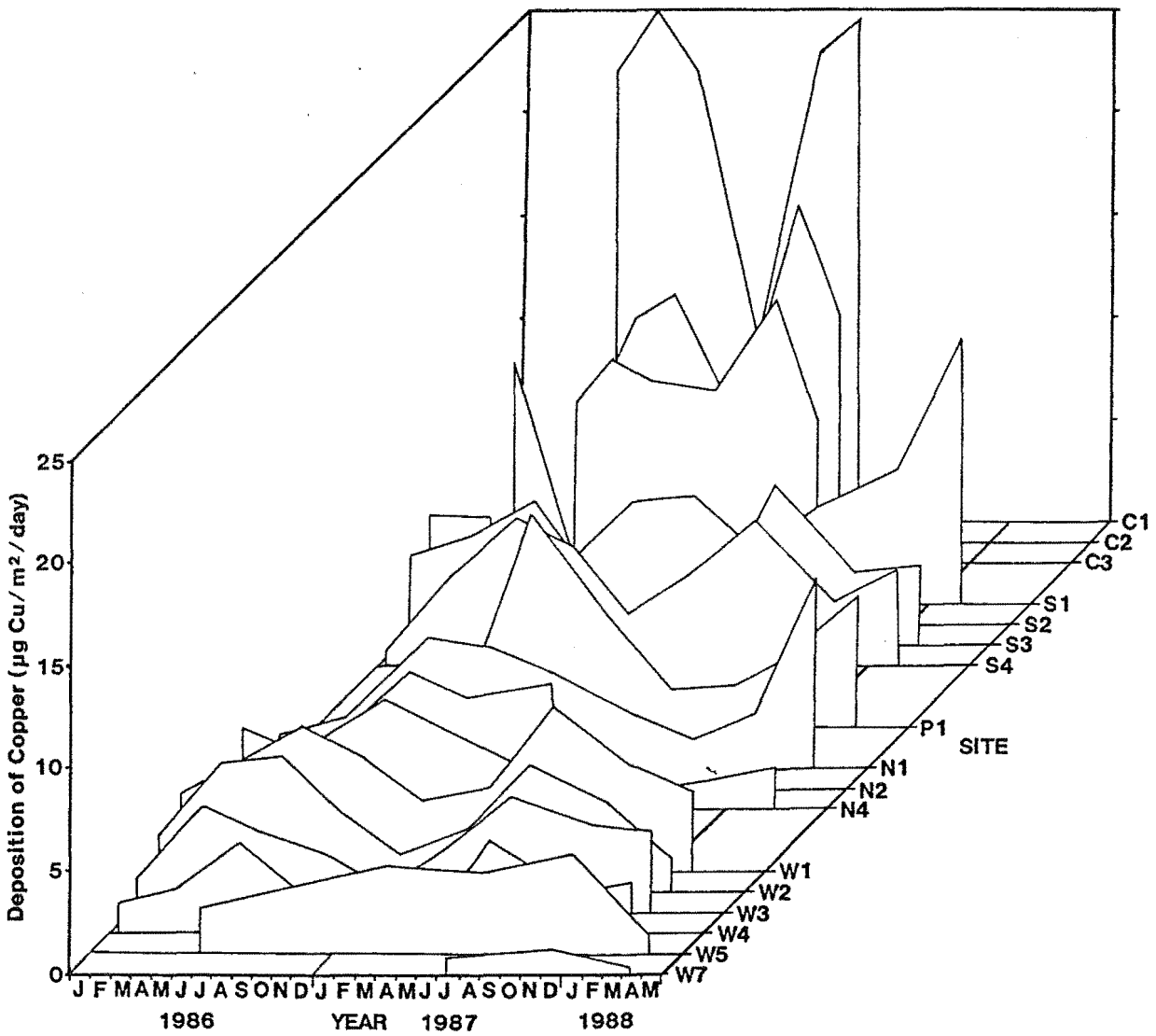

Figure 3.12 Seasonal variations in Cu deposition

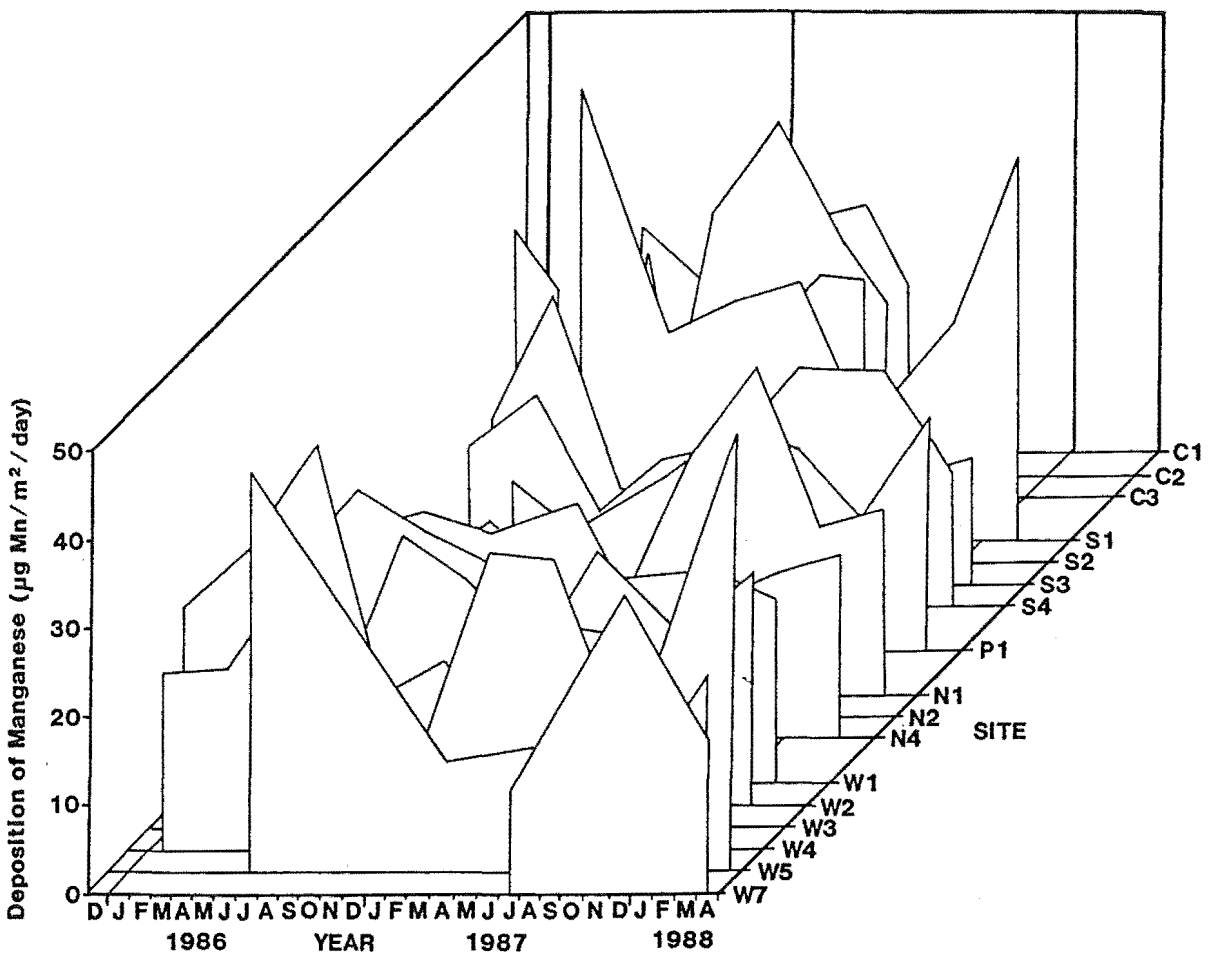

Figure 3.13 Seasonal variations in Mn deposition

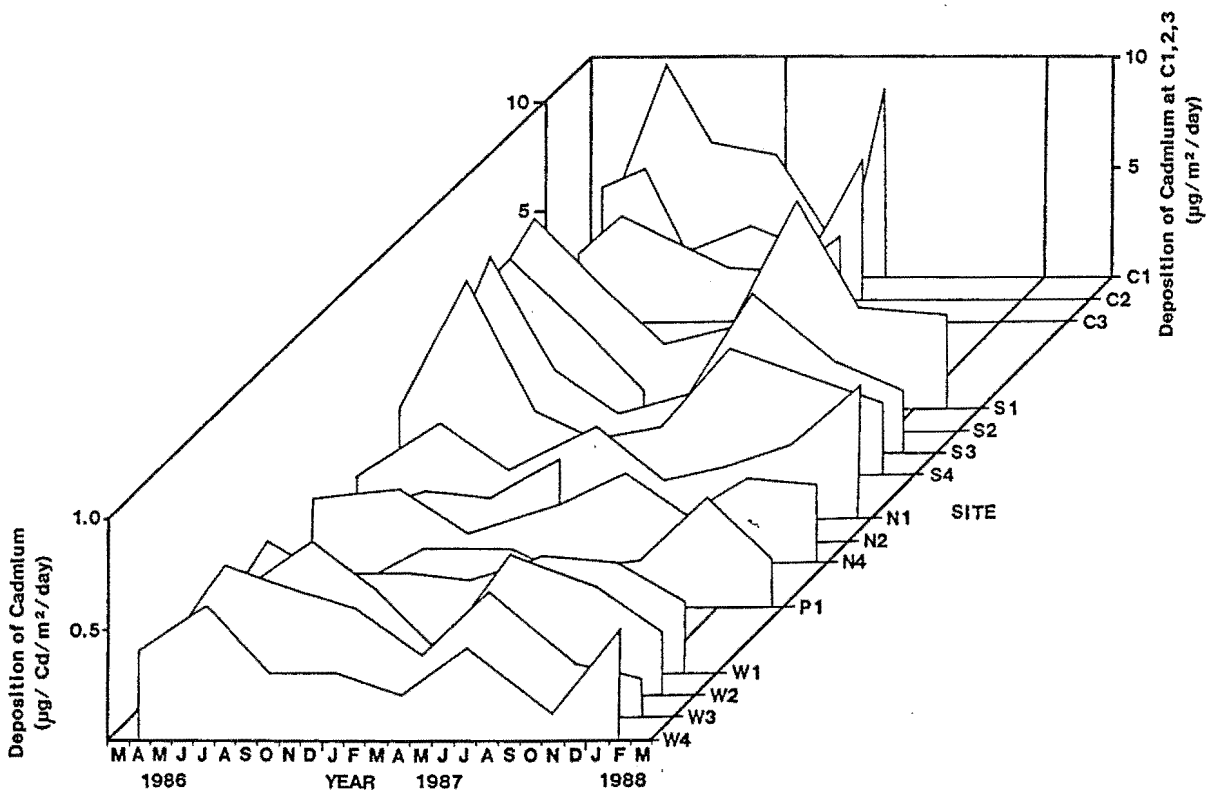

Figure 3.14 Seasonal variations in Cd deposition

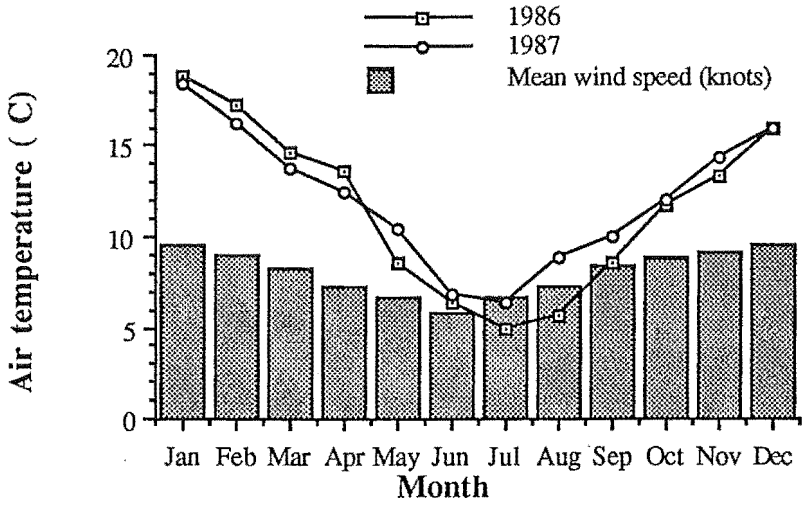

Figure 3.15 Seasonal variations in air temperature (°C) and mean wind speed (knots) at Christchurch airport

The data graphed in Figure 3.15 shows that the average windspeed in Christchurch has a winter minimum, as does air temperature. The Christchurch winter is characterised by relatively calm, cold conditions which produce low mixing heights and the buildup of airborne particulates. Simmonds et al. (1983) studied aerosol lead levels along Riccarton Road, Christchurch, and concluded that the difference between summer and winter concentrations was attributable to wind velocity. Sturman (1985) studied spatial patterns of smoke concentrations over Christchurch and concluded that the complex local windflow regime controlled the dispersion of smoke. In winter, low windspeeds result in an essentially stable, laminar airflow which acts to "shunt" air pollution around the city. Dispersion of the pollution by vertical mixing with cleaner air above is limited. In summer, higher windspeeds lead to more vertical mixing and hence dilution of pollutants. Another important parameter is the seasonal variation in the percentage of calm conditions. Analysis of meteorological data reveals that at Christchurch airport, it is calm 27.3% of the time in June, compared with only 10.2% in January.

Low temperatures are also associated with the buildup of high ambient concentrations , as the height of the mixing layer is temperature-dependent. Simmonds reports that this effect is usually submerged by the influence of wind speed.

Winter deposition maxima are very pronounced at the city sites. The rural sites downwind of the city (SW and W transect lines) also show the same pattern quite clearly,

indicating that these sites are influenced by urban air. The sites upwind and remote from the city do not show any particular seasonal trends, and are probably not strongly influenced by airmasses that have passed across the city.

Hence, it appears that transport of pollutants from urban to downwind rural areas is favoured by low wind speeds, because the pollutants are trapped in a layer of limited vertical extent and will eventually be transported horizontally to rural areas. Thus, mixing heights (which are a function of windspeed) appear to be the controlling meteorological variable in the seasonal variations observed.

3.3.5 Contributions of insoluble and soluble components to bulk deposition

For approximately one year of the sampling programme, both soluble and insoluble components of bulk deposition were measured, and the amount and pH of the rainfall recorded. Results are listed in full in the Appendix (Section 3.2). For all the data, histograms of the percentage of soluble metal found in each collector were constructed and are shown in Figures 3.16 to 3.20.

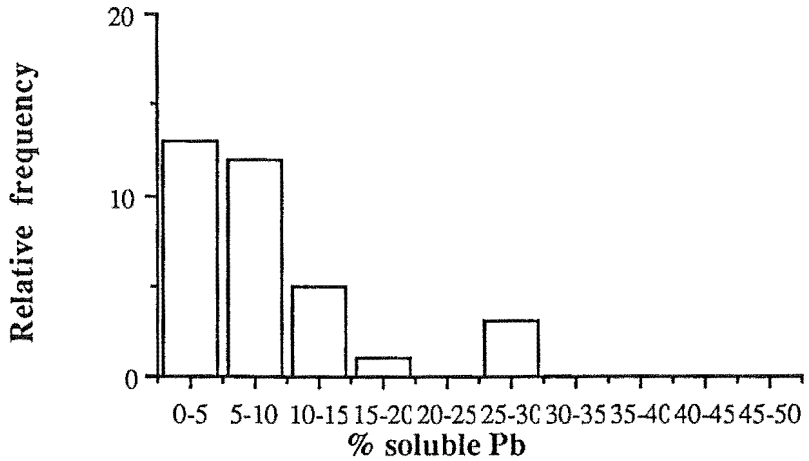

Figure 3.16 Percent soluble lead in bulk precipitation

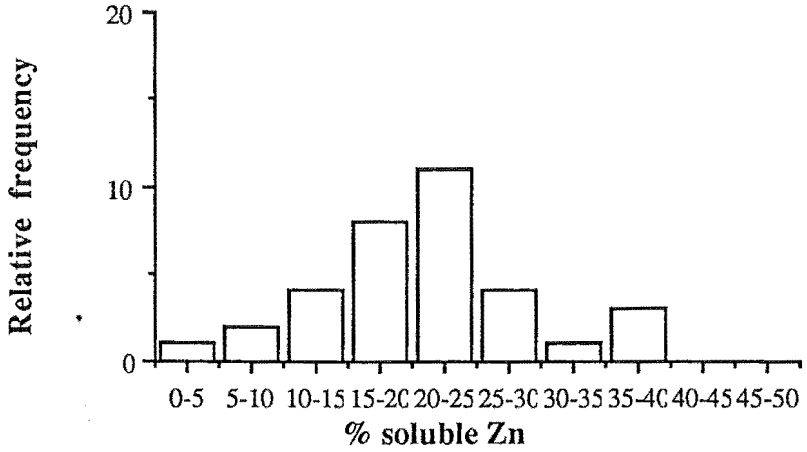

Figure 3.17 Percent soluble zinc in bulk precipitation

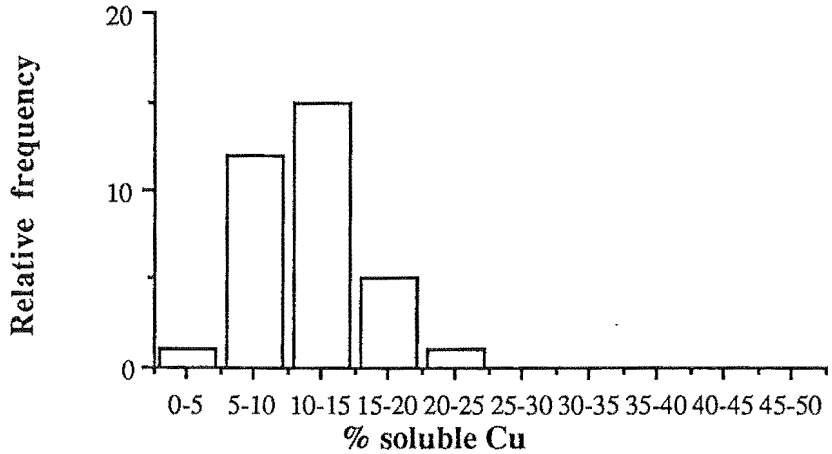

Figure 3.18 Percent soluble copper in bulk precipitation

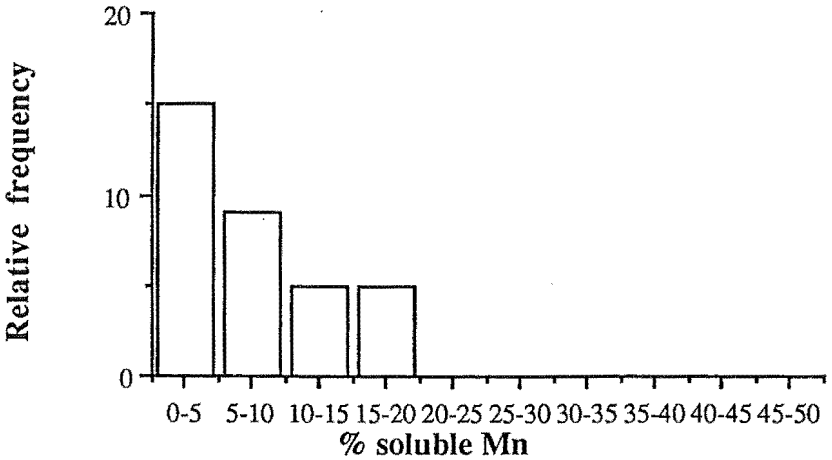

Figure 3.19 Percent soluble manganese in bulk precipitation

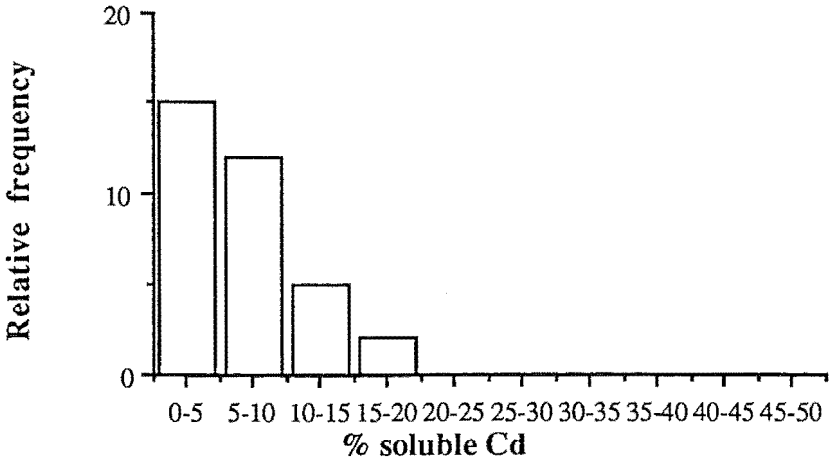

Figure 3.20 Percent soluble cadmium in bulk precipitation

As a brief summary of these histograms, Table 3.7 lists statistical parameters of these data.

Table 3.7 Statistical parameters for % soluble metals (N=34)

Element	X	σ_{n-1}	Median
Lead	8.1	7.8	5.3
Zinc	21.1	8.3	19.1
Copper	11.4	3.9	10.8
Manganese	7.3	5.6	4.5
Cadmium	6.0	4.0	4.5

Thus, zinc is the most soluble metal in bulk precipitation (around 20% soluble) followed by copper (10%) then lead, manganese and cadmium. Gatz and Chu (1986) reported a similar order of metal solubility in U.S. precipitation samples, except that cadmium was reported to be almost as soluble as zinc. The low solubility of cadmium found in this study is surprising. A possible explanation is that cadmium is present in the matrix of rubber particles arising from tyre wear.

The solubilities of metals in Canterbury deposition are lower than most reported overseas data. Gatz and Chu measured metal solubilities in wet, dry and bulk deposition and reported solubilities in bulk deposition to be 82% for zinc, 88% for cadmium, 38% for copper and 8% for lead. Obviously, these figures will vary depending on relative contributions of dry and wet to bulk deposition, as metal species appear to be much more soluble in wet deposition.

Canterbury generally experiences a dry climate with total annual rainfall being around 700 mm in Christchurch and increasing slightly towards the Main Divide. The period when the solubilities were assessed was particularly dry, with only 386 mm rain recorded from July 1987 to June 1988. Hence, dry deposition (with a lower proportion of soluble metals) probably makes a greater contribution to bulk fallout than in most reported studies (Andren and Lindberg, 1977; Jeffries and Snyder, 1980; Lindberg and Harriss, 1981; Lum and Kokotich, 1987).

An important influence on metal solubility in deposition (Gatz and Chu, 1986) is the pH of the rainfall which affects metal speciation, as in general, metal species are solubilised at low pH conditions. In this study, it was found that rainfall pH values were generally high, with an average of 6.1± 0.9, compared with values for United States precipitation of 4.0 to 5.5 (Gatz and Chu). Hence, the lower solubilities observed in the study may be a function of the higher pH of the rainwater.

The acidification of rainwater in many parts of the Northern Hemisphere due to anthropogenic emissions of sulphur and nitrogen oxides is well-documented (e.g. Likens et al, 1979; Elgmork et al. 1973; Pearce, 1982). The mean value of pH 6.1 found in this study is also higher than a weighted mean value for New Zealand rainfall of 5.6 (Holden and Clarkson, 1986). One explanation for the high pH values recorded in this study is that the mean may be weighted by samples collected in or near to Castle Hill Basin, which is composed of limestone. Hence airborne soil particles in the vicinity may raise the rainwater pH. Examination of the pH data listed in Appendix 3.2 shows that the average pH value for rainfall at sites W5 and W7 is in fact higher at pH 6.9.

The relationship between pH of rainwater and percent soluble metals was investigated further. Linear regressions were calculated for the percent soluble metal versus the pH for each metal. Relevant parameters of the regression are listed in Table 3.8; and the relationship is shown graphically for lead (as an example) in Figure 3.21. It should be noted from Table 3.8 that the more negative the slope of the fitted line, the greater the influence of pH on metal solubility. The r value indicates the goodness of fit of the line to the data points.

Table 3.8 Statistical parameters for linear fit to % soluble metal/pH relationship

Element	Slope of line	r (N=34)	Significance (N=34)
Pb	-7.0	0.856	Highly significant (p<0.001)
Zn	-5.9	0.670	Highly significant (p<0.001)
Cu	-2.0	0.498	Very significant (p<0.01)
Mn	-1.1	0.184	Not significant (p>0.1)
Cd	-1.6	0.369	Significant (p<0.05)

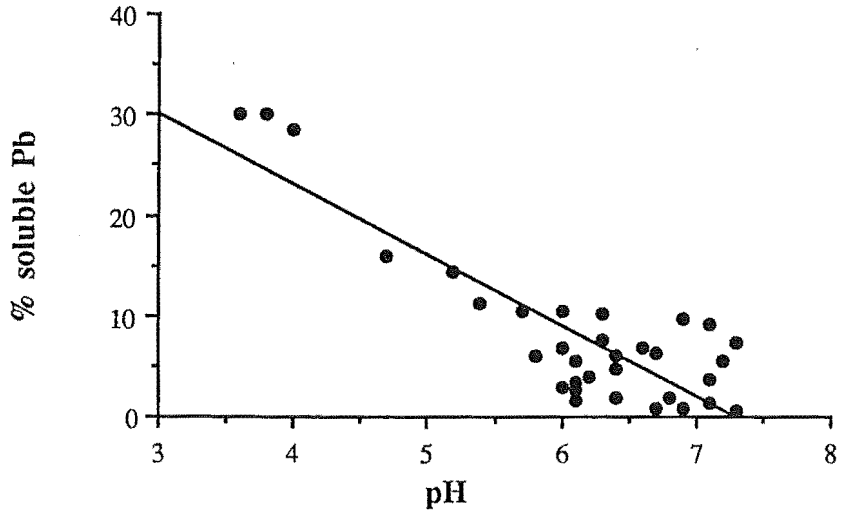

Figure 3.21 Percent soluble lead versus pH

Thus it can be seen that zinc and lead solubilities are the most pH-dependent. Copper and cadmium solubilities increase slightly with decreasing pH, and manganese solubility is least dependent on pH.

Another factor investigated was the total rainfall input to each collector. This was estimated from Meteorological Office data, measured at a network of stations over the region. It was found that there was little spatial variation in rainfall apart from a slight increase towards the Main Divide. Rainfall data from the station nearest to each collection site was used.

Linear regressions were calculated for rainfall amount versus the percentage of each metal present in soluble forms. It was found that the amount of rainfall appeared to have no systematic effect on metal solubility for any of the metals. The relationship is shown graphically for copper in Figure 3.22.

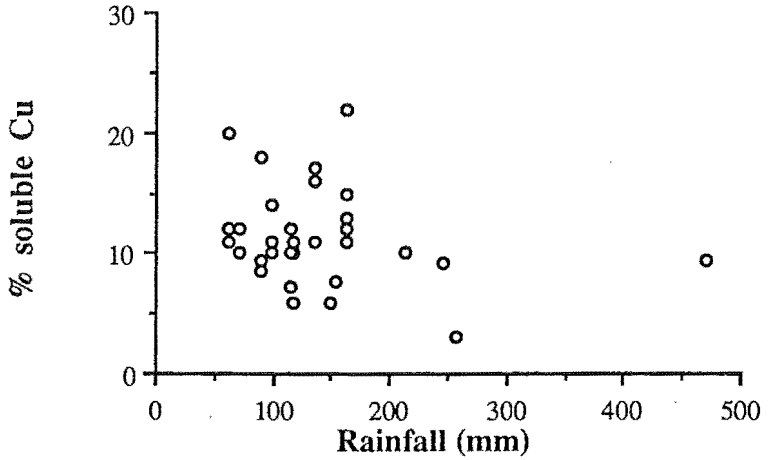

Figure 3.22 Percent soluble copper versus rainfall

At first glance, this result is surprising, as it might be predicted that the proportion of metals present in soluble forms would increase with increasing wet deposition, as wet deposition contains a higher proportion of soluble species (Gatz and Chu, 1986). The lack of such a trend in Canterbury precipitation is probably related to the minor role of wet fallout processes due to the relatively dry climate.

A potential problem in assessing proportions of soluble and insoluble species in bulk deposition is that free metal ions may adsorb onto the insoluble matter (especially clay minerals and hydrous iron/manganese oxides). The extent to which this process may have occurred is not known, and it would be necessary to collect wet and dry fallout separately to assess it. In natural waters, adsorption is thought to be limited, because of the existence of stable soluble metal-organic complexes rather than ionic forms (Florence, 1986).

To summarise the investigations into the relative proportions of soluble and insoluble metal species in bulk deposition, it was found that roughly 20% of zinc, 10% of copper, and 5-10% of lead, cadmium and manganese were present in soluble forms in Canterbury bulk precipitation. These values are low compared with reported overseas data. Possible explanations for low metal solubility in Canterbury include the high pH of the rainfall; the low rainfall of the region and hence the minor role played by wet removal processes; and a possibility of loss of metal ions in solution by adsorption onto the insoluble matter.

3.3.6 Sources of variability in deposition measurements

According to Galloway and Likens (1978), variability in deposition has three sources - analytical, sampling and spatial. The time-dependent nature of this study adds an extra source of variability.

Analytical variability is a precision barrier imposed by the measuring process. It includes recovery of the deposition from the collector, as well as digestion and analysis. Estimates of total analytical variability in this study were obtained by dispersing accurately-known amounts of standard reference material SD/N/1-2 within ten collectors, then recovering and analysing the spike. The variability was found to be in the order of 5-10%, and mostly arises from the precision limits of instrumental analysis. Flame AAS is considered to be accurate to within 3-5%, but the precision of graphite furnace AAS is limited to about ±10% due to the difficulty of reproducing 2µl sample injections.

Sampling variability is defined as the difference in precipitation composition between samples collected at the same site in adjacent collectors, and also necessarily includes analytical variability (Galloway and Likens, 1978). The magnitude of sampling variability was estimated by placing four collectors within an area of 1 m^2. The results of the analyses are presented in Table 3.9 for two separate trials.

Table 3.9 Sampling variability shown by 4 collectors within 1 m^2 area

Element	R.S.D.(%)		Moss-bag study*
	Run 1	Run 2	
Pb	11.2	13.5	16.7
Zn	7.2	8.9	11.9
Cu	19.3	23.9	-
Mn	6.5	4.7	-
Cd	20.6	19.2	16.3

* Little and Martin (1974)

It can be seen that sampling variability is larger than that arising from analytical procedures, but is generally less than 20%. Little and Martin (1974) obtained comparable values for moss-bag variability (Table 3.9). Values obtained by Galloway and Likens (1978) were higher, but related to collectors spread over a much larger area of 149 m^2.

Temporal variability was assessed from the data in Table 3.2, which lists deposition rates at each site averaged over the whole sampling period. It can be seen that

the relative standard deviations (the standard deviation divided by the mean) are generally larger than the sampling variability, with most R.S.D.'s lying between 20 and 60%.

The fourth type of variability, spatial, is actually an extension of the second type, but it arises from major differences in location between the collectors. The area of this study was around 5000 km^2. The amount of spatial variability depends on the type of metal. From the data in Table 3.2, it can be seen that cadmium deposition shows the greatest spatial variability, with data spanning over three orders of magnitude between urban, rural and remote locations. Lead and zinc deposition data spanned around two orders of magnitude, and copper was less variable, spanning slightly over one order of magnitude. Manganese deposition shows very little variability with location.

To summarise this section, spatial and temporal trends in metal deposition rates in Canterbury were studied. From the preceding discussion, it can be seen that for lead, zinc, copper and cadmium, spatial variability so greatly exceeds the other sources that its effect will be clearly seen. Seasonal variability is quite high at urban and downwind rural sites and hence stands out above analytical and sampling variability. However, at remote and upwind rural sites, seasonal variability is hardly distinguishable from analytical and sampling variability.

3.4 CONCLUSIONS

The main conclusions arising from the data discussed in this Chapter are stated briefly below.

a) Deposition fluxes of lead, zinc, copper and cadmium approximately followed exponential decay curves away from Christchurch city. Manganese deposition showed little spatial variation.

b) The prevailing wind direction (NE) affected the direction of dispersion of lead, zinc, copper and cadmium from the city.

c) Interelement correlation coefficients indicate a similar composite source for atmospheric lead, zinc, copper and cadmium and a different major source for manganese.

d) Enrichment factors (relative to soil) indicated that in the city, soil is not a major source of atmospheric lead, zinc, copper and cadmium, whereas at remote sites, atmospheric levels of these elements are mostly soil-derived.

e) Rates of deposition of zinc, copper and cadmium are lower in Canterbury than in most other countries at urban and rural locations. However, lead deposition in urban and rural sites is similar to or higher than in many overseas countries. This may be due to the high lead content of New Zealand petrol.

f) A reduction in lead deposition rates following the lowering of the lead content of New Zealand petrol appears to occur. However, it is difficult to separate this trend from seasonal variations.

g) Seasonal variations in deposition are large in the city, and at downwind rural sites. These variations are controlled by meteorological conditions, particularly windspeed, which determines the height of the mixing layer.

h) Compared with overseas studies, there were low proportions of metals occurring in soluble forms in bulk deposition. This may be due to the low rainfall in the area (hence the minor role played by wet removal processes) and the high pH of the rainfall.

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Chapter 4

Trace metals in topsoils

4.1 INTRODUCTION

Soil is a geochemical sink for terrestrially-deposited trace elements. This is because many trace metals are rapidly and completely fixed by soil components and will accumulate whereas processes that remove metals from soils (leaching, erosion, deflation) are slow by comparison. For instance, Purves (1972) found that applying the equivalent of 40 m of rainfall to columns of contaminated soil did not appreciably reduce their metal content, and concluded that " contamination of soil with respect to copper, lead and zinc appears to be virtually permanent". However, the mobility of metals in soils varies considerably with the nature of the soil and the metal speciation, as well as with climate and drainage. Some authors (e.g. Ward et al., 1977a; 1977b) report that leaching processes may act quite rapidly to lower elevated concentrations of some metals in contaminated soils.

It is of interest to compare the residence times of pollutants in the different environmental compartments. The atmosphere (discussed in Chapter 3) has a rapid turnover, due to the efficient removal processes (especially rainfall) and hence the average residence time of the atmospheric aerosol is usually considered to be about 14 days (Nriagu, 1978). In contrast, metals have a much longer residence time in soils. Nriagu (1980) reports an average global residence time of 3000 years for cadmium in soils. Kabata-Pendias and Pendias (1985) reported the following ranges of half-lives for metals in soils : lead 740 to 5900 years; zinc 70 to 150 years; copper 310 to 1500 years; and

cadmium 13 to 1100 years. Similarly, soils in Britain still show elevated soil concentrations of silver, lead, copper, tin, arsenic and mercury that date from mining in Roman times (Thornton and Abrahams, 1984). Lead appears to be particularly immobile in the soil profile (Harrison and Laxen, 1981; Khan, 1980; Ward et al., 1977).

Soil is heterogeneous by nature, and uncontaminated soils have large variations in their trace metal contents. Variability arises not only between soils formed from different geological parent materials, but also between sites in the same soil type, and between sample cores at a single site.

However, evidence from many studies (summarised in Purves, 1972; Purves, 1985; Davies, 1980) suggests that these natural variations are relatively small compared with anthropogenic contamination of soils with certain elements. Purves (1985) has stated that "it is possible to identify a soil as having an urban or rural origin from its composition with respect to the elements which are common urban contaminants". There is also evidence to show that some rural topsoils have elevated levels of lead, zinc and cadmium due to anthropogenic additions. Chamberlain (1983) calculated that rural topsoils in Britain (which has a long history of lead smelting) contain elevated levels of lead which can be quantitatively attributed to industrial emissions of lead as well as the combustion of leaded petrol.

The aim of the work described in this chapter was to assess to what extent atmospheric deposition affects topsoil composition at urban, rural and remote locations in Canterbury. Most studies suggest that urban soils will be strongly affected by anthropogenic additions, but effects on rural soils are less well-established. Topsoil cores were analysed for lead, zinc, copper, manganese and cadmium at the sites where deposition rates were measured (described in Chapter 3), and the relationship between topsoil concentrations and atmospheric deposition rate of these metals was examined.

It was also necessary to assess natural variations in composition of the soils of the Canterbury Plains. Work by McLaren et al. (1984) indicates that the soils of the Canterbury Plains are closely-related and relatively uniform in composition, as they originate from very similar parent materials. However, soils at sites W7 and P1 had

different geological origins, with W7 soil derived from limestone, and P1 soil derived from basalt.

4.2 EXPERIMENTAL

4.2.1 Sample collection and treatment

Because of the heterogeneous nature of soil, consideration must be given to sampling design. Tiller et al. (1975) reported that variability between cores at the same site is much greater than the variability between repeated analyses of the same core, and concluded that precision is improved by obtaining several cores at each location, rather than performing repeat analyses on a single core. Hence in this study, four cores at each site were taken.

Surface soil cores were extracted with a stainless steel hand corer of 35 mm internal diameter. Because of the dryness of the soils at many sites, some of the cores could only be obtained to around 6 cm depth. Prior to sampling, the corer was washed with hot soapy water, dilute acid and double-distilled water. Cores were transported to the laboratory in clean plastic bags. The cores were subdivided into 2 cm subsections, and the equivalent subsections at each site combined and well mixed to provide a composite sample representing each depth. Ten grams of field-moist soil were retained for E_h and pH measurements and the remainder was air-dried to constant weight at room temperature in an inert atmosphere box modified to contain clean air. The air-dry soil was crushed gently with a plastic-shielded stainless steel rolling-pin to pass through a 1 mm mesh nylon sieve, and stored in plastic jars

4.2.2 pH and E_h measurements

The procedures recommended by the New Zealand Soil Bureau (1972) were adopted. Ten grams of field-moist soil were stirred mechanically with 25 ml 0.01 M $CaCl_2$ and left to settle overnight. The pH of the supernatant solution was measured using a glass-calomel electrode couple, and the E_h measured using a platinum-calomel couple.

It should be noted that pH measurements obtained in this manner are arbitrary and operationally defined. The New Zealand Soil Bureau (1972) has pointed out that doubt

exists as to the significance of these measurements in terms of hydrogen-ion activity, because the results thus obtained reflect hydrogen-ion activity in the bulk solution adjacent to the electrode, rather than in the ion atmosphere around the soil particles. Hence, these measurements should be interpreted with regard to these limitations.

During this study, the following factors were investigated in obtaining pH values of soil solutions : the nature of the suspension medium, the ratio of soil to suspension medium and the amount of stirring. It was found that varying these factors did not affect the pH values greatly, although the reproducibility was improved with a $CaCl_2$ solution as the suspension medium.

Similarly, Bartlett (1981) and Blanchar and Marshall (1981) have pointed out that E_h, measured with a platinum electrode, is an unreliable estimate of the proportions of oxidised and reduced species in soils and waters. However, a measurement that is easy to obtain, reproducible, and at least qualitatively reflects redox conditions, is of value. E_h may be measured *in situ* , or by suspending soil in 0.01M $CaCl_2$.

4.2.3 Estimation of soil organic matter

Soil organic matter embraces the non-mineral fraction of the soil. The total organic matter is estimated from either a knowledge of total organic carbon, or from the weight loss upon ignition. Dawson (1982) has compared the two methods.

The estimation of total organic carbon involves oxidising all the carbon and measuring the volume of CO_2 evolved. The oxidation is carried out by wet or dry ashing, or by chromic acid decomposition. The figure thus obtained is multiplied by a factor of 1.72 to obtain total organic matter, as it is conventionally assumed that organic matter contains 58% carbon.

When soil is heated to 450°C, organic matter is oxidised to gaseous products and the soil loses mass. A highly significant correlation ($p<0.001$) exists between organic matter determined by weight loss upon ignition and organic matter determined by oxidisable carbon (Dawson, 1982) and total organic carbon is equal to 0.51 of the weight loss on ignition values (Dawson, 1982).

In this study, soil organic matter was estimated by the percent weight loss upon ignition. Accurately-weighed 0.2 g subsamples were ashed to constant weight at 450 °C.

4.2.4 Analytical Procedures

The choice of digestion technique will depend on the aims of the study. If the amount of soil metals actually available for plant uptake is to be assessed, then a weak partial extractant such as dilute acetic acid or EDTA (for organic-rich soils) is recommended (Khan, 1980). To measure total metals, it is necessary to use a stronger extractant, usually HF, to remove metals from within mineral lattices. Harrison and Laxen (1977) found that to obtain complete recovery of lead from soil, it was necessary to use a digestion mixture of 1:1 conc. HNO_3: 40% HF. However, if the soil is heavily contaminated with metals, a greater proportion of the metals will be in easily extractable form and HNO_3 will be of adequate efficiency.

In this study, the aim was to assess the total metal content of soils in locations with varying rates of metal deposition. At rural and remote locations, a substantial proportion of metals are likely to be bound in refractory forms. The recovery of metals from both a standard reference soil (Soil-5) and a well-homogenised Canterbury rural soil was investigated using the extractants 1:1 conc. HNO_3: 40% HF, and 4M HNO_3. The use of $HClO_4$ was avoided because of the risk of explosion. It was found that in all cases, the efficiency of the 4M HNO_3 extraction compared to a total HF/HNO_3 extraction was 98% for lead and cadmium; 95% for copper, 93% for zinc, and 91% for manganese, and this procedure was adopted due to its greater convenience.

Accurately-weighed 1 g subsamples of air-dried soil were boiled gently in 4M Analar HNO_3 for 30 minutes in covered 100 ml Pyrex beakers. The solutions were filtered through acid-washed Whatman No. 540 filter paper into 50 ml volumetric flasks. The solutions were analysed by flame AAS for lead, zinc, copper and manganese and by GFAAS for cadmium. Results were expressed as microgram of metal per gram of air-dried soil (μg/g).

The 4M HNO_3 extraction usually resulted in a coloured extract (ranging from yellow to dark brown) and background nonatomic absorption, presumably due to unoxidised organic matter in the solution, was significant. Another contribution to nonspecific absorption was molecular absorption due to the high salt content of the soil solution, and this high salt content also produced some physical blocking of the burner

which would interfere with the signal. The effects of these interferences were lessened if solutions were diluted, but the use of background correction was necessary in all cases.

For the analysis of cadmium by GFAAS, it was found to be advantageous to add H_3PO_4 as a matrix modifier. This practice produces a sharp cadmium peak at a higher temperature, as the volatile cadmium species are converted to the more refractory cadmium pyrophosphate (Brodie and Matousek, 1974).

4.3 RESULTS AND DISCUSSION

4.3.1 Concentrations of metals in Canterbury topsoils

For all the sites sampled, the soil description, concentrations of lead, zinc, copper, manganese and cadmium, together with pH, E_h and organic content are summarised in Table 4.1.

Table 4.1 Distribution of lead, zinc, copper, manganese and cadmium in Canterbury Plains soil profiles

Soil	Depth (cm)	Horizon	Pb	Zn	Cu	Mn	Cd	pH	E_h	%Org
a) W1					(μg/g)				(V)	
Southern Recent silt loam	0-2	Ah_1	18	52	8.7	384	.145	5.8	457	17.2
(Waimakariri series).Parent	2-4	Ah_1	18	56	9.0	372	.119	5.5	.509	13.1
material quartzofeldspathic	4-6	Ah_1	12	48	7.6	356	.097	5.4	.499	10.8
sediments.										
b) W2										
Southern Recent silt loam	0-2	Ah_1	11	60	8.9	408	.147	5.1	.479	19.1
(Waimakariri series).Parent	2-4	Ah_1	10	56	8.0	366	.113	5.1	.479	13.2
material quartzofeldspathic	4-6	Ah_1	11	48	8.1	351	.101	5.3	.471	14.2
sediments.										
c) W3										
Southern Recent silt loam	0-2	Ah_1	11	48	8.1	354	.107	5.6	.421	15.9
(Waimakariri series).Parent	2-4	Ah_1	11	45	7.6	342	.111	5.5	.465	14.9
material quartzofeldspathic	4-6	Ah_1	10	44	7.1	332	.101	5.0	.467	12.8
sediments.	6-8	Ah_2	11	46	7.3	348	.091	5.7	.479	16.9
	8-10	Ah_2	12	45	7.2	344	.072	5.8	.484	15.9

d) W4

Southern Recent silt loam	0-2	Ah_1	6.8	46	6.7	342	.068	5.9	.567	15.0
(Waimakariri series).Parent	2-4	Ah_1	7.2	42	6.4	318	.066	5.4	.505	12.0
material quartzofeldspathic	4-6	Ah_1	8.2	36	5.2	292	.052	5.7	.454	9.1
sediments.	6-8	Ah_1	7.2	41	5.7	306	.059	5.8	.434	6.1
	8-10	Ah_2	8.4	42	6.6	302	.039	5.7	.469	10.1

e) W5

Southern Recent silt loam	0-2	Ah_1	10	49	6.7	400	.066	6.0	.493	10.3
(Kowai Series).Parent	2-4	Ah_1	14	65	9.4	412	.084	5.6	.452	14.6
material quartzofeldspathic	4-6	Ah_1	16	77	13	318	.106	5.2	.455	17.7
sediments										

f) W6

Southern Yellow-Grey	0-2	Ah_1	17	57	12	430	.059	5.3	.510	20.8
Earth (Kakahu Series).	2-4	Ah_1	14	57	12	370	.056	5.4	.499	13.3
material quartzofeldspathic	4-6	Ah_1	14	57	12	302	.060	5.1	.491	12.1
sediments										

g) W7

High country yellow-	0-2	Ah_1	16	47	8.4	522	.517	7.1	.584	11.1
brown earth (Kaikoura	2-4	Ah_1	16	45	8.7	510	.521	7.0	.612	9.0
series).Parent material	4-6	Ah_1	15	47	9.0	508	.468	7.1	.594	8.8
limestone	6-8	Ah_1	15	46	9.0	534	.472	7.1	.528	10.6
	8-10	Ah_1	18	39	7.5	526	.446	7.2	.521	14.9

h) S1

Southern Recent silt loam	0-2	Ah_1	16	54	7.0	442	.087	5.6	.454	20.1
(Templeton Series).Parent	2-4	Ah_1	14	55	6.7	452	.123	5.5	.501	15.5
material quartzofeldspathic	4-6	Ah_1	13	52	6.0	438	.142	5.7	.504	12.2
sediments	6-8	Ah_1	14	56	8.4	434	.143	5.2	.505	13.1
	8-10	Ah_2	14	53	7.0	452	.121	5.0	.516	10.1

i) S3

Southern Recent silt loam	0-2	Ah_1	16	51	5.5	550	.081	6.0	.445	20.0
(Templeton Series).Parent	2-4	Ah_1	18	45	5.7	444	.082	5.7	.467	13.9
material quartzofeldspathic	4-6	Ah_1	17	44	4.7	471	.081	5.6	.461	8.6
sediments										

j) S4

Southern Recent silt loam	0-2	Ah_1	21	65	6.3	598	.097	5.7	.482	19.7
(Templeton Series).Parent	2-4	Ah_1	18	61	5.9	522	.098	5.9	.473	10.0
material quartzofeldspathic	4-6	Ah_1	17	53	4.8	464	.094	5.1	.515	6.4
sediments										

k) N1

Southern Recent silt loam	0-2	Ah_1	16	58	11	386	.162	5.7	.422	16.9
(Waimakariri series).Parent	2-4	Ah_1	17	59	11	360	.101	5.9	.452	17.0
material quartzofeldspathic	4-6	Ah_1	15	56	10	380	.138	5.7	.478	13.1
sediments	6-8	Ah_1	13	57	11	340	.122	5.9	.476	8.8

l) N2

Southern Recent silt loam	0-2	Ah_1	13	22	7.6	368	.144	6.1	.391	19.1
(Waimakariri series).Parent	2-4	Ah_1	12	21	7.7	332	.194	6.4	.427	14.2
material quartzofeldspathic	4-6	Ah_1	12	22	8.5	390	.211	5.4	.460	15.3
sediments										

m) N4

Southern Recent silt loam	0-2	Ah_1	6.6	62	5.1	442	.070	5.7	.402	20.0
(Waimakariri series).Parent	2-4	Ah_1	6.5	47	4.0	398	.066	5.6	.419	19.0
material quartzofeldspathic	4-6	Ah_1	6.0	52	4.3	400	.063	5.7	.417	14.9
sediments										

n) P1

Brown Granular Loam	0-2	Ah_1	13	51	9.1	1372	.184	4.6	.503	15.7
(Summit Series).Parent	2-4	Ah_1	11	55	11	1131	.131	4.4	.509	11.6
material andesitic basalt	4-6	Ah_1	11	55	9.2	1010	.129	4.6	.477	9.9
and diorite	6-8	Ah_1	9.3	51	9.8	1226	.072	4.5	.482	8.8
	8-10	Ah_1	7.2	54	9.6	1216	.040	4.5	.499	8.9

o) C1

Southern Recent silt loam	0-2	Ah_1	1720	950	48	396	.839	5.6	.462	22.3
(Tai Tapu series).Parent	2-4	Ah_1	1350	715	47	382	.754	5.3	.452	19.4
material quartzofeldspathic	4-6	Ah_1	2140	640	48	372	.632	5.2	.453	25.6
sediments										

p) C2

Southern Recent silt loam	0-2	Ah_1	33	79	12	250	.114	5.9	.323	20.9
(Tai Tapu series).Parent	2-4	Ah_1	38	77	11	269	.111	5.8	.325	11.2
material quartzofeldspathic	4-6	Ah_1	33	74	12	243	.092	6.2	.348	8.9
sediments. Poor drainage	6-8	Ah_1	31	79	10	262	.083	6.0	.332	9.0
	8-10	Ah_2	35	75	8.0	251	.088	6.0	.333	7.9

q) C3

Southern Recent silt loam	0-2	Ah_1	29	68	9.9	568	.171	5.3	.482	15.3
(Waimakariri series).Parent	2-4	Ah_1	28	67	9.3	540	.173	5.0	.541	12.1
material quartzofeldspathic	4-6	Ah_1	36	78	12	632	.179	5.4	.543	18.8
sediments.	6-8	Ah_1	30	70	10	550	.170	5.0	.532	16.8

The data summarised in Table 4.1 will be discussed for each element.

a) Lead Apart from the urban soil cores, lead concentrations in the rural and remote topsoils do not show much variation with location, with a range of 5.1 to 21 μg/g, and a mean concentration of 14±4 μg/g. Differences in parent material of the soils do not have much effect, as the lead concentrations of the soils at site W7 (derived from limestone) and P1(andesitic basalt) are not distinguishable from soils derived from quartzofeldspathic sediments. Thus, a background value of around 14 μg/g Pb for Canterbury Plains soils may be assigned, although it must be remembered that the 4M HNO_3 extraction is not quite 100% efficient.

This background concentration of lead is very similar to reported overseas levels, although as Nriagu (1978) pointed out, it is impossible to assign a meaningful "average" global concentration because of the natural heterogeneity of lead distribution in soils. Nriagu reported that the average background soil lead levels in a variety of countries ranged from 10 to 37 μg/g, and obtained a weighted (on the basis of land area) global average of 17 μg/g Pb, which is the same as the average crustal lead concentration. Adriano (1986) reports an average of 20 μg/g in soils worldwide.

The urban soil cores show enrichment over the rural and remote soil lead concentrations, with inner city site C1 enriched around 150 times, and the suburban soils C2 and C3 enriched around 2 to 3 times. The accumulation of lead in urban soils due to anthropogenic emissions is very well-documented. Nriagu (1978), Chow (1973), Davies (1980), Purves (1985) and Khan (1980) provide comprehensive reviews. The main conclusions are that urban soils are frequently enriched with lead due to deposition from automobile exhaust emissions, smelters and coal burning. In Christchurch, an additional source of lead in soils is very important : this is the weathering of leaded paint off older wooden houses (Jordan and Hogan, 1975).

At site C1, the lead content of the soil was around 2000 μg/g, which is higher than values for typical urban soils reported by Nriagu (1978). It is true that roadside soils can contain lead concentrations of up to 6000 μg/g (e.g. Harrison, 1981), but site C1 was located around 30 metres from the nearest road, and the typical exponential decrease of lead with depth (e.g. Ward et al., 1975a) was not observed in core C1. Hence, it seems

likely that an additional source of lead (most likely weathered paint) is contributing. A mass-balance approach to this question will be considered in the following section.

b) Zinc The zinc content of rural and remote soils was found to span a range of 21 to 65 μg/g, with a mean concentration of 52±11 μg/g. The zinc content did not vary systematically with location, nor was the effect of parent material noticeable. The mean level of 52 μg/g is fairly similar to reported values of 40 to 58 μg/g (Shuman, 1980) and 90 μg/g (Adriano, 1986) for uncontaminated soils. In urban soil C1, a concentration of 950 μg/g was measured, which is enriched around 20 times over the rural and remote soils. Slight enrichments were observed in the suburban soils.

c) Copper The copper content of rural and remote soils spanned a range from 4.3 to 13 μg/g, with an average level of 7.9±2.0 μg/g. Similarly to zinc and lead, varying the distance from Christchurch, and the type of parent material, did not seem to affect the soil composition, except that the basaltic soils at site P1 contained slightly more copper (9.6±0.4 μg/g).

Compared with overseas values, copper levels in Canterbury Plains rural soils are low. Adriano (1986) reports a mean value of 30 μg/g, and Thornton (1979) reports values of 20 μg/g in British soils, 18 μg/g in the U.S.A. and 16 to 32 μg/g in the U.S.S.R. Copper-deficient soils are reported in many areas; these usually contain less than 10 μg/g copper, and are often associated with sandy soils. Thus, it appears that Canterbury Plains soils are in fact slightly copper-deficient. This is consistent with a study of the EDTA-extractable copper, manganese and zinc content of Canterbury Plains rural topsoil by McLaren et al.(1984). These authors reported that levels of extractable copper and zinc in Canterbury soils are very low, and that these soils are potentially copper and zinc deficient. However, total zinc levels determined in the present study were not noticeably low.

The copper concentrations in the urban soils were enriched over the background levels, with an approximately six-fold enrichment in the core at site C1, and slight enrichments in the suburban soils.

d) Manganese The distribution of manganese in Canterbury Plains topsoils differed from the other elements, as there was no enrichment of manganese in urban

topsoil. but the effect of parent material was very strong. The soils derived from quartzofeldspathic sediments (including urban soils) had a mean manganese content of 433±79 μg/g, but the calcareous soil at site W7 contained 520 μg/g, and the basaltic soil at site P1 contained 1180 μg/g Mn. These values are quite similar to ones reported by Adriano (1986), with manganese concentrations reported as 460 μg/g in sandstone-derived soils, 620 μg/g in limestone-derived soils, and 390 to 1620 μg/g in soils derived from igneous rock.

Another factor is the redox status of the soil, as manganese oxides are solubilised under reducing conditions. The most reducing soil in this study was at site C2, in Riccarton. This soil had the most negative E_h values (around 0.3 V) and also the lowest level of manganese in the surface samples.

e) Cadmium The cadmium content of the rural and remote soils spanned quite a wide range from 0.039 to 0.345 μg/g, with a mean of 0.12±0.08 μg/g. This mean value is lower than reported mean cadmium concentrations in uncontaminated soils of 0.2 μg/g (Nriagu, 1980) and 0.35 μg/g (Adriano, 1986). The cadmium content of the limestone derived soil was significantly higher than the average, at 0.52 μg/g. The urban soil at site C1 is enriched around 7 times over rural and remote soils, but the suburban soils show only very slight enrichment.

Another point of interest is the distribution of metals within the soil profiles. The non-enriched remote and rural soil profiles show no strong trends with depth, although there does appear to be a slight decrease with depth in many of the profiles, especially for cadmium. In the upper 6 cm of the heavily contaminated soil C1, levels of zinc and cadmium decline, copper remains about the same, and the lead concentration increases with depth. However, since the sample cores at site C1 were taken from a garden, it is probable that the original soil profile has been disturbed.

In summary, it is clear that in accordance with the findings of Purves (1985), the trace metal compositions of non-urban soils are determined by their parent material. However, urban soils are clearly distinguishable on the basis of their levels of lead, zinc, copper and cadmium (but not manganese), which override natural variations.

4.3.2 Relationship between rates of deposition and topsoil composition

Linear correlation coefficients between measured rates of deposition and topsoil composition were calculated a) for all sites, b) omitting sites with soils of different parent material W7 and P1, c) omitting city sites C1, C2, C3, and d) omitting C1,C2,C3, W7 and P1. The results are presented in Table 4.2.

Table 4.2 Linear regressions for topsoil metal content (μg/g) versus deposition rate at each site

Element	a)All sites	b)All sites - W7, P1	c)All sites - C1, C2, C3	d)All sites - W7, P1, C1, C2,C3
N	17	15	14	12
Pb	0.860 h	0.884 h	0.283 n	0.493 n
Zn	0.889 h	0.892 h	0.224 n	0.378 n
Cu	0.861 h	0.880 h	0.158 n	0.167 n
Mn	0.089 n	0.237 n	0.063 n	0.237 n
Cd	0.558 s	0.699 v	0.383 n	0.055 n

Significance h - highly significant ($p<0.001$)
v - very significant ($p<0.01$)
s - significant ($p<0.02$)
n - not significant ($p>0.1$)

From the data listed in Table 4.2, it can be seen (from column a) that highly significant linear correlations exist between rates of deposition and topsoil composition for lead, zinc and copper. A significant relationship exists for cadmium, but there is no relationship for manganese. However, these high correlations are mostly due to the strong weighting effect of the city sites. If these data points are omitted from the regression calculation (columns c and d in Table 4.2) none of the relationships are significant. This result is not surprising, as it was seen in the previous section that compositions of rural and remote soils are not related to their distance from the city. Hence, rates of deposition in rural and remote soils are too low to produce changes in topsoil composition that are visible above natural variations.

Slight improvements in correlation coefficients were obtained by omitting the sites with different geological origins (column b in Table 4.2). A large increase in r occurred for cadmium, because of the high concentration of cadmium naturally present in the

calcareous soil at site W7, and also for manganese, because of the anomalous high concentration of manganese in the basaltic soil at site P1.

If the sites of different soil type were omitted from the regression calculation for the non-city sites (column d in Table 4.2), the correlation coefficients also increase : in the case of lead, the relationship is almost significant. Thus, atmospherically-deposited lead may have a slight effect on rural topsoil composition.

Work by Chamberlain (1983) suggests that anthropogenic additions of lead have affected rural topsoils in Britain, although the largest component of the increase is attributed to lead from extensive mining and smelting of lead ores rather from combustion of leaded petrol. Chamberlain calculated that on average in British rural soils, a cumulative fallout of 3.4 g Pb/m^2 of topsoil has been added from anthropogenic activities, with 3 g attributed to smelting operations (particularly in the 18th and 19th centuries when emission controls were less effective), and 0.4 g from leaded petrol combustion since 1946. Assuming that the deposited lead has been mixed to 15 cm depth and that the bulk density of soil is 1 g/cm^3, this additional lead would produce an increase in topsoil lead of 20 μg/g, of which about 2.6 μg/g is from petrol combustion.

Since present rural rates of lead deposition in Britain and Canterbury are quite similar (about 60 $\mu g/m^2$/day), a similar increase might be expected in rural Canterbury soils. However, evidence for such an increase is not very strong, as the lead concentrations in rural soils do not show much tendency to decrease away from Christchurch. It is likely that any increases are masked by natural variations in lead concentrations.

In the inner city site C1, the present average rate of lead deposition is about 340 $\mu g/m^2$/day, or 124 mg/m^2/year. If the assumptions made by Chamberlain are used, a cumulative fallout of 2.48 g/m^2 from petrol lead would increase the lead content of the top 15 cm of soil by about 17 μg/g. The contribution from historical industrial emissions is not known, but even if it was of comparable magnitude to the cumulative amount contributed by exhaust emissions, it is very unlikely that the observed topsoil lead levels of 2000 μg/g at site C1 could be accounted for by atmospheric deposition. The most probable source of lead to this inner-city soil is the weathering of leaded paint from the

adjacent house. It is well-established (Jordan and Hogan, 1975) that the soils surrounding many old wooden houses in Christchurch contain elevated lead concentrations, typically in the range 1000 to 3000 μg/g.

Similar calculations for zinc at site C1 indicate that the principal source of the elevated zinc levels in the inner-city topsoil (950 μg/g) is unlikely to be atmospheric input. A likely nonatmospheric source of zinc to urban soils is rainwater runoff from galvanised iron roofing materials (Purves, 1985).

For the suburban sites C2 and C3, cumulative lead fallout from exhaust emissions could account for around 8 μg/g in topsoils if Chamberlain's assumptions are used. However, it should be noted that the depth of the mixing layer assumed by Chamberlain (15 cm) applies to agricultural soils. Other authors (e.g. Ward et al., 1977b; Harrison and Laxen, 1981) report that deposited lead is usually confined to the top 5 cm in undisturbed soils. In this case, the cumulative fallout at sites C2 and C3, confined to a narrower mixing layer, could produce an increase of around 24 μg/g in the suburban topsoils. The measured lead concentrations in the suburban topsoils are elevated by roughly this amount over levels typical of background soils (14 μg/g).

4.3.3 Sources of variability in soil composition

Tiller et al. (1975) distinguished four sources of variability that contribute to natural diversity in soil composition : between determinations in cores (D), between cores in sites (C), between sites in soils (S), and between soil types (T). Type D is equivalent to analytical variability, type C is sampling variability and types S and T are forms of spatial variability.

Analytical variability was assessed by performing repeated analyses on soil from a single core, as well as on a reference soil (I.A.E.A. Soil-5). It was found that the precision of analyses was slightly higher for the reference material (presumably because of more thorough homogenisation), but in all cases, the variability was less than 5%.

The sampling variability (for cores at the same site) was found to lie between 5 and 15% , with zinc, lead and cadmium determinations tending to be the most reproducible (5-7%) and manganese the least (14-17%). At site W6 (Lake Rubicon) 12 soil cores were taken at various locations around the lake, over an area of approximately 4

ha. Over this distance, the variability in metal concentrations was found to be larger than sampling variability, ranging from 22% for zinc to 30% for manganese. A contributing factor towards this divergence in composition may be drainage, as the cores taken from from the steepest slopes also showed the lowest concentrations of all five metals, presumably due to downslope leaching.

4.4 CONCLUSION

It is clear that the main differences in composition between the soils of the Canterbury Plains are between soils in urban and rural locations. This conclusion is in agreement with most published work. There is good correlation between topsoil metal concentrations and rates of atmospheric deposition when all sites are included, but rough calculations show that additional nonatmospheric sources of lead and zinc are required to account for the observed topsoil concentrations in the inner city site C1. In rural areas, the effects of atmospherically-deposited metals are not visible above natural variations, but there is limited evidence to suggest that lead levels in Canterbury Plains topsoils may be affected by atmospheric deposition.

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Chapter 5

Historical monitoring by tree-ring analysis

5.1 INTRODUCTION

In the previous two chapters, variations in atmospheric deposition rates of lead, zinc, copper, manganese and cadmium at urban, rural and remote sites in Canterbury were investigated. In this chapter, atmospheric deposition in the Christchurch urban area will be examined from a historical perspective, using tree-ring analysis.

5.1.1 The study of tree rings

The principles of historical monitoring of heavy metals were discussed in Chapter 1. Trees are dissimilar to other depositional media such as sediments, ice and peat deposits. Because they are living organisms, the relationship between atmospheric concentrations of pollutants and concentrations recorded in the annual rings of trees is complex and poorly understood.

However, the ability of trees to record external influences is well-known. For instance, climatologists have related patterns in ring width and density to past climatic conditions (Fritts, 1976). It also appears that annual rings respond to their chemical, as well as physical, environment. For example, a decrease of $^{13}C/^{12}C$ ratios observed in ring wood formed in recent years (Leavitt, 1988; Freyer, 1981) is considered to reflect the changing isotope ratio in the atmospheric CO_2 pool; this is ascribed to fossil fuel burning which adds ^{13}C-depleted CO_2. More recently, many authors have suggested that the heavy metal content of tree rings may be used to monitor heavy metal deposition histories.

a) Previous studies Lead has been the metal which has received the most attention, particularly in relation to lead emissions from motor vehicles. In Sweden, Kardell and Larsson (1978) found a correlation between lead concentrations in oak tree xylem and petrol consumption, following the addition of lead to Swedish petrol in 1946. Other authors have observed similar trends in different tree species (Ward et al., 1974; Baes and Ragsdale, 1981; Hall et al., 1975).

It appears, however, that species-response is highly variable. For example, Baes and Ragsdale studied the ring wood of three different tree species in a forest beside a major traffic artery (30,000 vehicles day^{-1}) in Atlanta, Georgia. These authors reported that hickory (*Carya spp.*) and oak (*Quercus alba*) trees showed significantly elevated concentrations of lead after 1923, when lead was added to petrol, but tulip (*Liriodendron tulipifera*) trees did not. Also, the concentration of lead in recent hickory xylem was around 100 times greater than in recent oak xylem, indicating a much greater tendency by hickory trees to accumulate lead. Burton (1985) has recently reviewed studies on heavy metal concentrations in tree-ring xylem, and also concludes that in general, differences between species in both their tendency to accumulate heavy metals, and their sensitivity of response to lead pollution, are very pronounced.

Studies have also been carried out specifically related to industrial emissions. In Japan, Ishizaki et al. (1970) analysed sugi (*Cryptomeria japonica*)trees for cadmium and zinc to determine whether cadmium contamination, responsible for Itai-Itai disease in the locality, had originated from a zinc mine upstream of the trees. Elevated metal concentrations were found in the annual rings of two trees from the contaminated area, compared with those in five trees from similar sites along unpolluted rivers. In another Japanese study, Suzuki (1975) measured zinc and cadmium levels in the annual rings of sugi trees near a zinc refinery, and reported that cadmium levels appeared to be the most useful historical indicator of refinery emissions. Lead, zinc, copper and cadmium have all been studied extensively (e.g. Dutot and Faucherre, 1979; Symeonides, 1979; Robitaille, 1981;) and occasionally other metals, such as silver, mercury, rubidium, iron, chromium and gold, have been measured (e.g. Sheppard and Funk, 1975).

The techniques that have been used to analyse the chemical composition of tree rings can be classified as either destructive or non-destructive. The destructive techniques involve either dry or wet ashing of the sample, dissolution and analysis by GFAAS or ICP-AES. The main problem associated with these techniques is that a relatively large mass of sample is required as metal levels are low, and this gives poor temporal resolution of the rings (typically 5-10 years). ICP-AES has advantages over GFAAS because of its multielement capacity and improved detection limit (Feng, 1984).

The main nondestructive techniques are INAA and PIXE. INAA has a similar resolving power to the destructive techniques. Its main disadvantage is that it does not detect lead and cadmium. PIXE has found favour with many analysts as it is capable of measuring individual growth rings (e.g. Valkovic et al., 1979; Legge et al., 1984; Amato, 1988) and is probably the most promising technique currently available.

b) Problems in interpretation of dendrochemical data The data obtained from dendrochemical analysis should be interpreted cautiously as many of the factors which influence the uptake and binding of metals in wood are poorly understood (Lepp, 1975). There also appears to be a difference between the response of hardwood and softwood species to metal uptake and binding (Baes and Ragsdale, 1981; Hampp and Holl, 1974). It is thought that coniferous species (softwoods) are inherently more suitable than angiosperm species (hardwoods) for recording metal uptake (Legge et al., 1984; Symeonides, 1981; Bondietti, 1988), due to the more primitive nature of conifer wood. In particular, ray cells, which are thought to be an excretion route for toxic products (Stewart, 1966), are less well-developed in conifers. Hence, toxic heavy metals are more likely to accumulate in the xylem of conifers.

Conifers, however, are diffuse-porous and the sapwood, or zone of xylem conduction, is more likely to involve several rings instead of being confined to the outermost ring. A recent model proposed by Bondietti et al. (1988) considers the sapwood to be "a moving zone of cation exchange columns which conduct water and solutes at varying efficiencies because of age, blockages and other factors". Hence metals taken up in a particular year may also appear in rings formed in earlier years. For instance, Bondietti et al. (1988) report that fallout ^{90}Sr appears in red spruce ring wood

formed ten years prior to the fallout period. The number of rings affected depends on the age and size of the tree but does not usually appear to involve more than around 5-10 rings.

An additional problem associated with dendrochemical analysis is concerned with the accuracy of dating growth rings. In an individual core, inaccuracies may arise if growth rings are absent or if more than one ring is formed annually (Norton and Ogden, 1987). Such anomalous rings place tree-ring sequences out of order. Crossdating, which involves matching of similar ring-width patterns between different trees, should identify anomalous rings and is likely to be the most accurate approach to dating (Fritts, 1976). However, cross-dating works only when a common factor limits the growth of the trees, and, as in this study, this is not always the case. Alternatively, by working with groups of 10 to 20 rings, effects of single-ring errors are likely to be unimportant (D.A. Norton, pers. comm.).

5.1.2 Aim of this study

This study aimed to assess the potential of annual growth rings for studying the heavy metal pollution history of Christchurch. The native conifer kahikatea (*Dacrycarpus dacrydioides*) was chosen for investigation; its long lifespan (up to 600 years) was considered to be particularly suitable for historical monitoring as it enabled pre-European conditions in Christchurch to be studied.The urban sampling site, Riccarton Bush, is a small remnant of lowland kahikatea forest. As it is the only forest of its type remaining in lowland Canterbury, a comparable stand of kahikatea trees was chosen as a background control sited on a terrace near the Wanganui river, South Westland. Concentrations of the heavy metals lead, zinc, copper, cadmium and manganese were determined in the tree ring wood.

The entry routes of atmospheric metals into tree ring wood were also investigated in this study. Burton (1985) noted that although the potential of annual rings to act as historical monitors of atmospheric metal burdens has been amply demonstrated, modes of entry of atmospheric metals are still poorly understood.

5.2 EXPERIMENTAL

5.2.1 Sampling sites

a) Riccarton Bush Riccarton Bush, Christchurch, is a remnant of kahikatea forest located approximately 2.5 km west of Central Christchurch (Figure 3.2). The stand is approximately 5.4 ha in area. Its southern boundary is located approximately 80 m north of Riccarton Road, a busy two-lane thoroughfare averaging around 20,000 cars per day since 1970 (Canterbury United Council, pers. comm.). It is surrounded by residential areas, with the Addington/Hornby industrial areas 2 km to the south.

Kahikatea (*Dacrycarpus dacrydioides*) is the dominant emergent tree over a mixed canopy of broadleaved trees and epiphytes. The kahikateas appear even-aged (300-400 years old).

b) Wanganui River Flats This site was chosen and sampled by David A. Norton of the School of Forestry, University of Canterbury. It is located at map reference NZMS 1 S63 094141 and is approximately 15 m above sea level. The forest is similar to Riccarton Bush, although probably of younger age. Kahikatea is again the dominant tree. Since this site is located 10 km west of State Highway 6 (a low-volume highway) and at least 50 km from any industrial activity, significant anthropogenic sources of heavy metals are absent and these trees may be considered to be from a 'background' location.

5.2.2 Sample collection and treatment

a) Tree cores Large, straight-boled trees were selected for coring. Three trees were randomly chosen form each site; 1 tree from each was cored in two different radial positions to assess radial variability in heavy metal distribution. Cores were extracted at 1 m height with a Swedish 4.3 mm stainless steel increment borer. In the laboratory, the borer was cleaned with AR acetone to remove grease, and then with weak acid and double-distilled water. Samples were immediately sealed in dry acid-washed plastic straws for storage and transport to the laboratory. A core for dating was also taken from each tree immediately adjacent to the sample core. The dating core was accurately dated under magnification in the School of Forestry.

The analytical sample cores were opened in the Clean Room and handled on Class 100-rated laminar-flow benches. Each core was cut into decade intervals by comparison with the dating core. Occasionally, annual rings were too close together for a decade segment to provide sufficient mass for analysis and 20-year intervals were used in these cases.

Several authors (Baes and Ragsdale, 1981; Berish and Ragsdale, 1985; Clegg and Wigley, 1988 unpublished report) have recommended washing the core segments (usually with 0.1 mol l^{-1} HNO_3 for 30 seconds) to remove surface contamination. A potential problem with this procedure is that metals may be leached from the cores. In this study, it was recognised that contamination of the xylem could result from the transfer of metal from the outer surfaces of the trees to the xylem by the corer, as it is well-known that bark is an efficient collector of airborne particulates. Hence a decision was made to wash the core segments, and each segment was immersed for 5 seconds in 0.1 mol l^{-1} Aristar HNO_3 then rinsed briefly with running Milli-Q water. The segments were air-dried to constant weight in 10 ml Pyrex beakers.

b) Bark and foliage Samples of bark and foliage were collected from kahikatea trees at both sites. The bark samples were collected at 1 m height. Unfortunately, the foliage of mature trees is out of reach so, in Riccarton Bush, branches that had fallen to the ground were sampled. The Westland samples were shot down from the canopy with a shotgun. The samples, which were stored in clean plastic bags, were handled using disposable plastic gloves.

Samples were dried to constant weight at 80°C in a clean oven. No attempt was made to wash the samples.

c) Soil Cores Surface soil samples were obtained from both sites to a depth of 10 cm with a stainless steel hand auger. These samples were divided into 2 cm sections and air-dried to constant weight in an inert atmosphere box modified to contain clean air.

Two 1-m deep cores were obtained from Riccarton Bush with a stainless steel mechanical auger. The cores were partially pedologically classified by field tests (see Appendix) and then divided into 5 cm sections. Separate 10 g field-moist subsamples of

each section were retained for E_h and pH measurements; the remainder was air-dried to constant weight.

The air-dry soil was crushed gently with a plastic-shielded stainless steel rolling-pin to pass through a 1 mm mesh nylon sieve, and stored in plastic jars.

5.2.3 Analytical methods

a) Wood, bark and foliage In general, wet-ashing is recommended for the dissolution of biological materials (Sansoni and Panday, 1981) because it achieves decomposition of the organic matrix at lower temperatures than dry-ashing and thus avoids the loss of volatile analyte compounds. However, it was found that to destroy the resistant cellulose matrix of the ring wood, dry-ashing was necessary. Dry-ashing, followed by dissolution in 2M HNO_3, was found to give good recoveries of the biological standard reference materials IAEA V-9 and V-10.

Thus, the air-dried samples were ashed at 400°C, and the residues obtained dissolved in Aristar HNO_3. The usual dissolution procedure was for a small volume (125 µl) of concentrated HNO_3 to be added to the ash, the solution warmed under an infrared heat lamp and made up to a final acid strength of 2 mol l^{-1}. For bark and foliage samples, sufficient material (1-2 g) was used so that lead, copper and cadmium could be measured by flame AAS. However, because of the small amount of the ring wood core sections available (50-80 mg) it was necessary to use electrothermal atomisation of the sample to detect lead, copper and cadmium. Concentrations of zinc and manganese were high enough to allow flame atomisation.

b) Soil Procedures for soil analysis have been discussed in detail in Chapter 4.

i) E_h and pH Procedures recommended by the NZ Soil Bureau Laboratory Methods (1972) were adopted. Ten grams of field-moist soil was mechanically stirred with 25 ml 0.01M $CaCl_2$ and left to settle overnight. The pH of the supernatant solution was measured using a glass/calomel electrode couple; E_h was measured using a platinum/calomel couple.

ii) 4M HNO_3 - extractable metals Accurately-weighed 1 g subsamples of air-dried soil were boiled in 4M Analar HNO_3 for 30 minutes and filtered through Whatman 540 filter paper into 50 ml volumetric flasks to a final acid strength of 2 mol l^{-1}. The

solutions were analysed by AAS with flame atomisation for lead, zinc, copper and manganese and graphite furnace atomisation for cadmium.

iii) *Plant-available metals* To estimate "plant-available" metals, 10 g subsamples of air-dried soil were shaken overnight with 25 ml of 0.04M Na_2EDTA (adjusted to pH 6 with NaOH). The solutions were centrifuged at 3000 RPM for 30 minutes and the supernatant solution analysed for lead, zinc, copper, manganese and cadmium as above.

iv) *Organic content* The organic content of the soil was estimated by the percent weight loss upon ignition. Accurately weighed 0.2 g samples were heated to 450°C in Pyrex 10 ml beakers for 24 hours, cooled in a dessicator and reweighed to constant weight.

5.3 RESULTS AND DISCUSSION

5.3.1 Levels of metals in kahikatea ring wood

Raw data for all the cores analysed are listed in the Appendix. Two representative cores from each site are shown graphically in Figures 5.1 to 5.5; the remaining data illustrated the same trends but have been omitted for clarity. Some of the data for Riccarton Bush Tree 2 is incomplete as some samples were accidentally lost. Each data point represents the concentration of the metal in each segment (usually 10 years) plotted at the midpoint of the time interval.

The accuracy of the data has been estimated by measurements on the biological standard reference materials cotton cellulose and hay (Section 2.5). The precision is limited by the reproducibility of the instrumental techniques; around $\pm 5\%$ for flame AAS measurements and $\pm 10\%$ for graphite furnace measurements. The yearly dating of the cores was accurate to within 1-2 years.

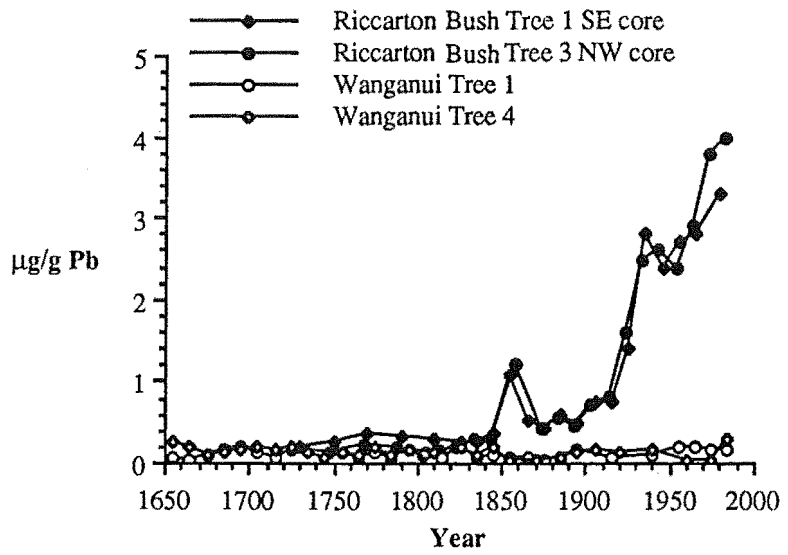

Figure 5.1 Lead content of kahikatea ring wood

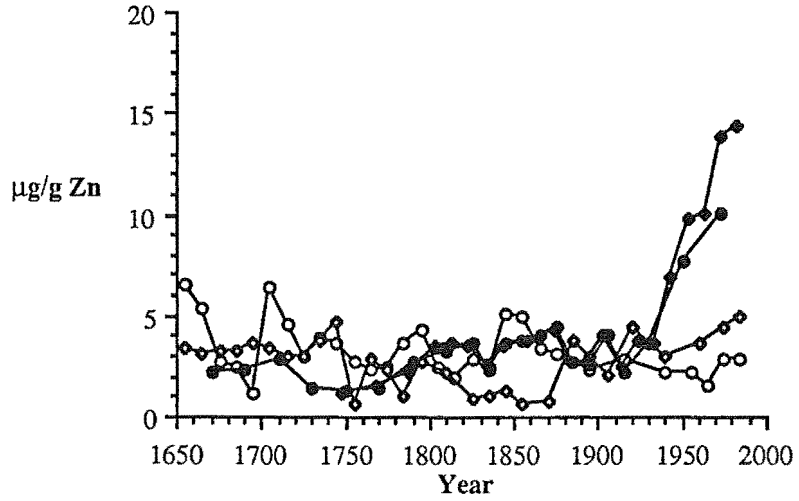

Figure 5.2 Zinc content of kahikatea ring wood

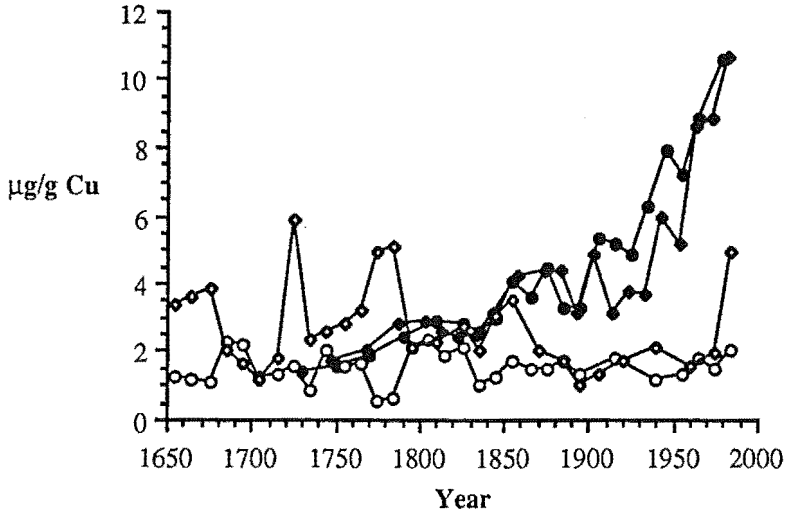

Figure 5.3 Copper content of kahikatea ring wood

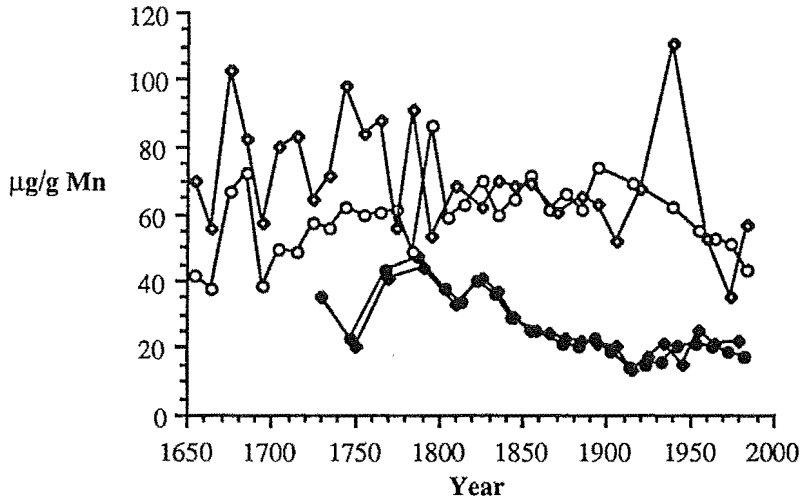

Figure 5.4 Manganese content of kahikatea ring wood

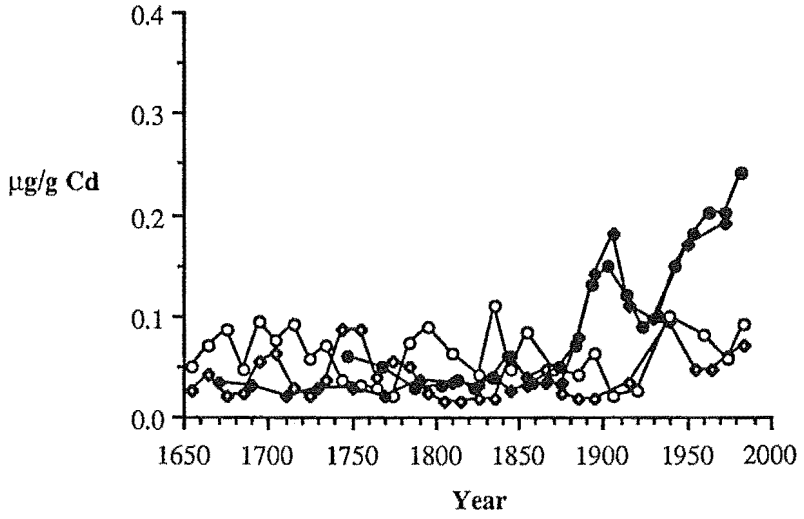

Figure 5.5 Cadmium content of kahikatea ring wood

A general feature of the data displayed in Figures 5.1 to 5.5 is the good agreement in metal concentrations for the pairs of trees, especially at Riccarton Bush. This provides confidence in both the accuracy of the tree-ring dating and in the general sensitivity of the Riccarton Bush kahikatea trees to environmental levels of heavy metals. The trends apparent from Figures 5.1 to 5.5 will be discussed in more detail below.

a) Lead Lead concentrations (Fig 5.1) show the greatest elevation in the urban trees. From similar baseline values, the urban and background cores begin to diverge around 1850, with a small peak around 1860. A rapid acceleration is evident around 1920, and rapid accumulation continues until the present, apart from a plateau roughly

corresponding to the years 1935-1950. Hence, there has been an increase in the external supply of lead to urban trees. Possible atmospheric sources of this increased lead are industrial emissions, weathering of leaded paint, and combustion of leaded petrol.

There are several past and present sources of industrial lead in Christchurch. A battery factory and associated lead smelter on the banks of the Heathcote river in Woolston have been known to elevate lead levels in the sediments of the Heathcote river and its estuary (Purchase and Fergusson, 1986). Morrison (1948) has noted that there was an industrial boom in Woolston in the 1870's and 1880's; and a general acceleration in industrial development in Christchurch in the 1930's. It is difficult to determine with any certainty the amount of lead emitted from industrial activity. However, industrial emissions typically only affect localised areas. Ward, Roberts and Brooks (1977) found that beyond 90 m from a battery factory in Auckland, New Zealand, the distribution of lead was dominated by motor vehicle exhaust lead. Davies (1980) reviewed published reports and concluded that metal contamination is most severe within around 3 km of a point source and declines progressively until background concentrations in soils are reached between 10 and 15 km from the source. Thus, as Riccarton Bush is located 8 km to the west of Woolston, it is unlikely that these sources could account for the major accumulation of lead in the kahikatea ring wood. The lead peak appearing in ring wood between 1860 and 1870 may well be related to the industrial boom around this time.

Scott (1983) estimated the possible contribution to the environmental lead burden of the weathering of leaded paint from older houses in Christchurch. He concluded that weathering could have contributed up to 70 x 10^3 kg/year lead in the 1940's and 1950's, but has probably contributed a negligible amount since 1960. At this time, leaded paints were phased out and it is assumed that old lead paint will have been painted over with lead-free paints. Up to 16 x 10^3 kg/year could be released annually by sandblasting but in recent years, this has been a carefully controlled process. Since most of the lead from paint is immobilised in the topsoil close to the painted surface (Jordan and Hogan, 1975), paint weathering is considered to be an insignificant source of atmospheric lead over the whole city.

The combustion of leaded petrol is probably the dominant source of lead to the Christchurch atmosphere. Day (1976) estimated, on the basis of emission data, that in Christchurch, 99% of anthropogenic lead emissions originate from petrol lead. This is consistent with overseas estimates of 98% (National Academy of Sciences, 1971) in the U.S.A. and 90% in the U.K. (Fussell, 1970). The slightly higher figure for Christchurch could easily be due to the higher lead content (0.84 g l^{-1}) used in NZ premium grade petrol until July 1986.

The time of the rapid lead accumulation also suggests that petrol lead is the dominant source. Tetra-ethyl lead was first manufactured as an octane booster in the U.S.A. (Nickerson, 1954), and was first used in New Zealand petrol in 1933 (Coleridge, 1973). Accumulation of lead becomes apparent in wood formed in the 1920's ; this is consistent with the suggested xylem conduction mechanism in softwoods (Bondietti et al., 1988). Similar trends in lead accumulation were also observed by Ward, Brooks and Reeves (1974) in a study of the effects of petrol lead on roadside trees in Palmerston North, New Zealand. They attributed the slowing of the upward trend observed in 1935-1950 ring wood to petrol shortages after World War II. They also observed a rapid increase in accumulation from the mid-1960's, corresponding to a doubling in motor-vehicle registrations from 1961 to 1971. In Christchurch, data available from the Canterbury United Council (N. Pilling, pers. comm.) indicates that Riccarton road traffic increased from 7700 cars/day in 1958 to 14,900 in 1966. Numbers stabilised in 1970 at around 20,000 cars/day, which is the capacity of the road during the working day.

A very significant correlation ($R=0.931$, $p<0.01$, $N=7$) exists between lead accumulation in Riccarton Bush kahikatea ring wood and total New Zealand oil consumption over the period 1924-1984. This relationship is shown graphically in Figure 5.6. Although total New Zealand oil consumption provides only a crude indication of the likely volume of vehicle exhaust emissions in the vicinity of Riccarton Bush, it is probably the best easily available indicator (New Zealand Official Yearbook, 1988-89).

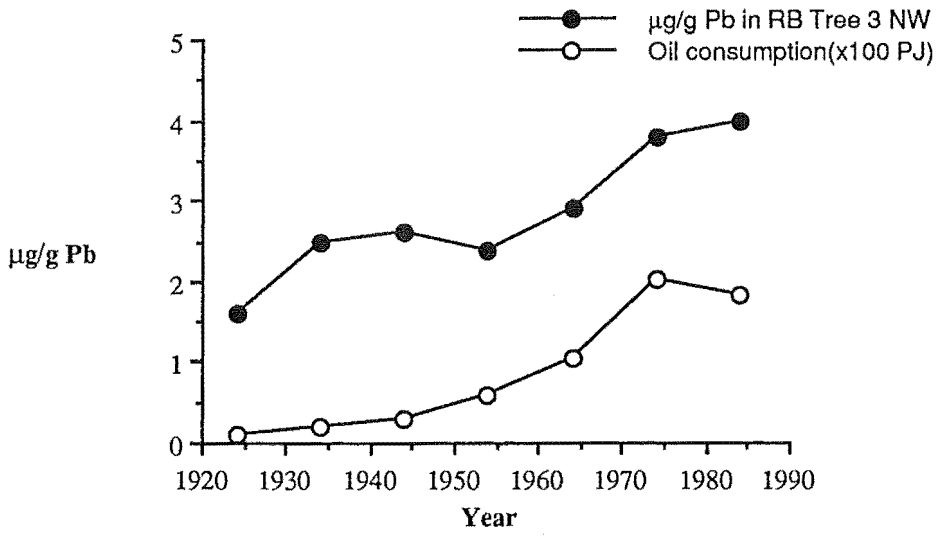

Figure 5.6 Pb accumulation in kahikatea 3 from Riccarton Bush versus total New Zealand oil consumption 1924 - 1984.

Thus, it seems likely that the observed accumulation of lead in Riccarton Bush kahikatea ring wood from 1920 onward can be explained in terms of lead originating from motor vehicle emissions, with a possible, but unknown, contribution from general industrial sources associated with the development of Christchurch. The earlier peak around 1860 may be related to the industrial boom at that time.

b) Zinc, copper and cadmium In the urban cores, zinc, copper and cadmium levels show moderate elevation over baseline levels (Figures 5.2, 5.3 and 5.5) with an approximately three-fold elevation beginning around 1940. This accumulation is probably due to increased industrial emissions of these elements, as discussed previously. Specific sources of these metals to the Christchurch atmosphere are likely to be zinc (and cadmium by association) from a galvanising works in Hornby and weathering of galvanised iron roofing, cadmium from an electroplating works in Woolston and copper used in fungicidal and insecticidal sprays. More general sources include coal, oil and wood burning; refuse incineration; automobile and tyre wear.

c) Manganese Manganese (Fig 5.4) shows quite different behaviour. Levels in urban trees are around half of those in the background trees. A possible explanation for this relates to soil acidity differences between the two sites; the acidity of the Westland soil was around pH 4.0 whereas the Riccarton Bush soil was around pH 6.0. Although many factors can affect soil manganese availability to plants, "in general the amount of

extractable manganese is inversely related to soil pH" (Adriano, 1986). Bromfield (1987) found that the availability of manganese increases rapidly when the soil pH is below 5.4. Another feature of Figure 5.4 is the decline since about 1850 of manganese levels in the urban ring wood. This is thought to be related to the progressive draining of the swampy land underlying Christchurch leading to more oxidising conditions in the soil and therefore less soluble forms of manganese prevailing (such as MnO_2). Hercus (1948) indicates that the draining of the Riccarton swamps began in the 1850's.

In summary, it appears that relative to trees from a background site, kahikatea trees in Riccarton Bush, Christchurch, contain elevated levels of lead, zinc, copper and cadmium in their ring wood, and that these accumulations of heavy metals can be related to known historical emissions of these elements to the atmosphere. In contrast, manganese concentrations in ring wood are controlled by soil conditions (E_h and pH), rather than an external supply.

5.3.2 Sources of variability

a) Within trees This was assessed by coring several trees on opposite sides. Results for lead and manganese are displayed in Figures 5.7 and 5.8. These were typical of all the data and show that radial variability is small. Unfortunately, a statistical comparison is not possible because the data is not paired.

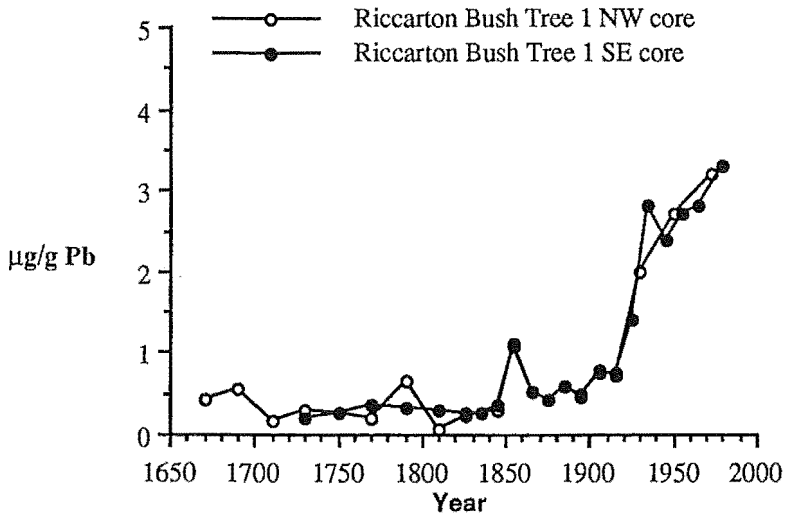

Figure 5.7 Radial variation in Pb concentration

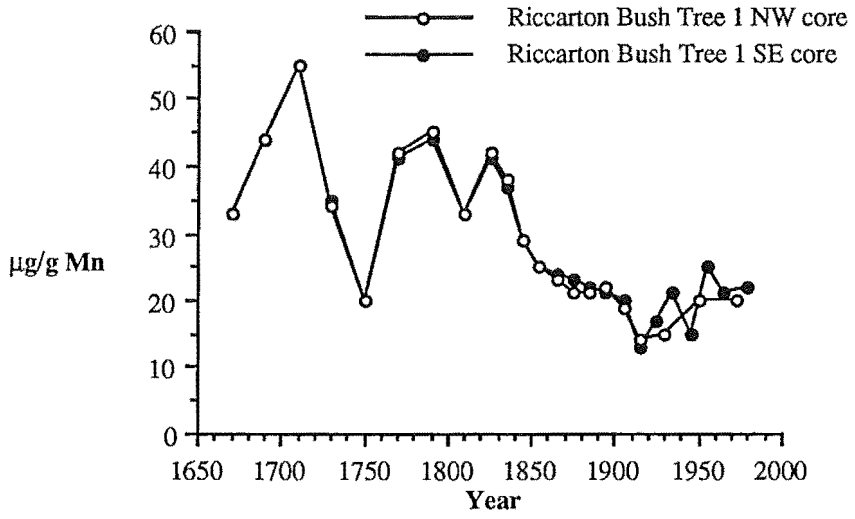

Figure 5.8 Radial variation in Mn concentration

b) Between trees It can be seen from Figures 5.1 to 5.5 that cores from different trees at the same site show some natural variation. This is smaller, however, than the major trends observed and the patterns of accumulation are consistent between trees.

5.3.3 Neutron activation/Flame AAS comparison

It was decided to analyse two cores from the same tree by completely independent methods. One core was measured by the method described in Section 5.2.3 and the other was submitted to CSIRO Fuel Technology Division in Sydney for instrumental neutron activation analysis (INAA). This technique does not detect lead and cadmium (or copper, at long counting times) but manganese and zinc were measured and compared. An assessment of the accuracy of INAA was made by submitting a sample of standard reference material cotton cellulose along with the sample cores. This is discussed in Section 2.2.4.

Results for the two cores are presented in Figures 5.9 and 5.10. It can be seen that for zinc, the agreement between the two methods is good, and the variability is similar to the natural amount of variability found within trees. For manganese, the amounts measured by INAA are larger than the FAAS levels. This difference was also found for the standard reference material submitted with the core. A possible explanation is that there is a contribution to ^{56}Mn from ^{56}Fe also present in the samples (Fergusson

and Ryan, 1984). To correct for this, it would be necessary to estimate this contribution and subtract it from the high values.

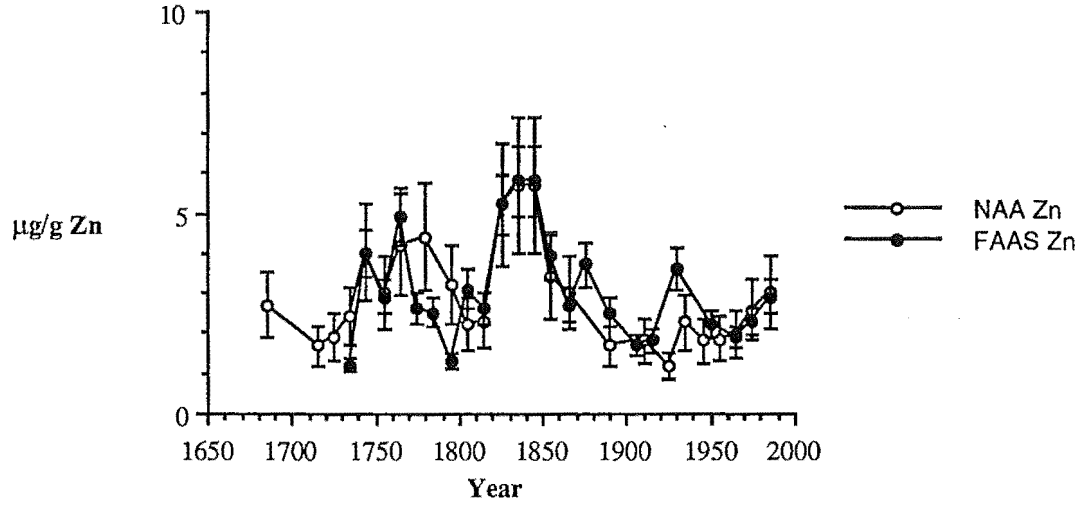

Figure 5.9 Comparison between INAA and FAAS measurements of zinc content of two cores from Wanganui River Flats Tree 2.

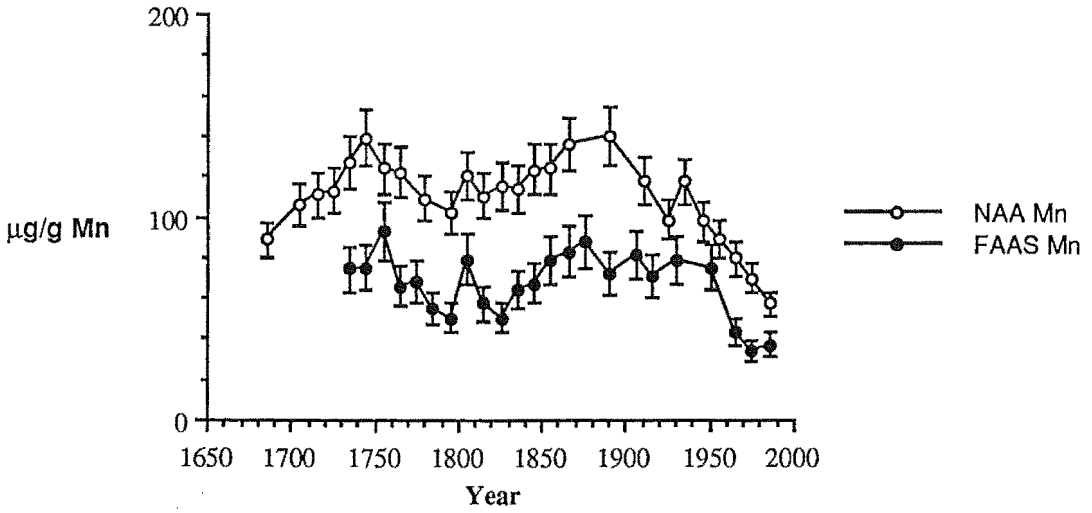

Figure 5.10 Comparison between INAA and FAAS measurements of manganese content of two cores from Wanganui River Flats Tree 2.

Hence, comparison of flame AAS measurements with those obtained by INAA provides additional confidence that the measuring process for heavy metals in tree ring wood adopted in this thesis is reliable.

5.3.4 Effect of fluctuations in annual ring size

Berish and Ragsdale (1985) noted that apparent concentration increases can result from constant elemental deposition into smaller annual rings. Most authors appear to overlook this possibility. To ensure that the metal accumulation patterns discussed previously do not result from fluctuations in annual ring width, results were also calculated on a μg/year basis and compared to the μg/g data. It was found that in all cases, μg/year results correlated highly significantly with μg/g results. Fluctuations in annual ring size must be regarded as a source of variability although to some extent the practice of analysing samples in decade intervals will even out yearly fluctuations.

5.3.5 Pathways of heavy metals into ring wood

The uptake, transport and deposition processes of heavy metals within trees have been reviewed by Lepp (1975) who concluded that there are two main possibilities for the entry of atmospheric metals into annual growth rings. Metals may become elevated in soil following wet or dry deposition and be taken up through the root system into the xylem. Another possibility is the direct deposition of metals onto the tree surfaces (bark and foliage) by deposition, impaction and diffusion, followed by transport into the ring wood. There is evidence from radiotracer studies (Lepp and Dollard, 1974) that this 'lateral' transport occurs.

For metals strongly immobilised in soil, such as lead, uptake from soil seemed an unlikely pathway to produce the observed elevation of lead in the tree rings. In order to investigate both pathways, soil, bark and foliage samples were analysed from both sites.

Soil core descriptions, E_h and pH data, organic content, and 'total' and plant-available metal concentrations were measured for each soil core and are listed in full in the Appendix for the two 1-m deep cores collected from Riccarton Bush. The 'total' metal content, estimated by a 4M HNO_3 extraction, is shown in Figure 5.11. For comparison, typical total metals (estimated by the same method) for Canterbury Plains rural soils are presented in Table 5.1. These estimates are based on data discussed in Chapter 4.

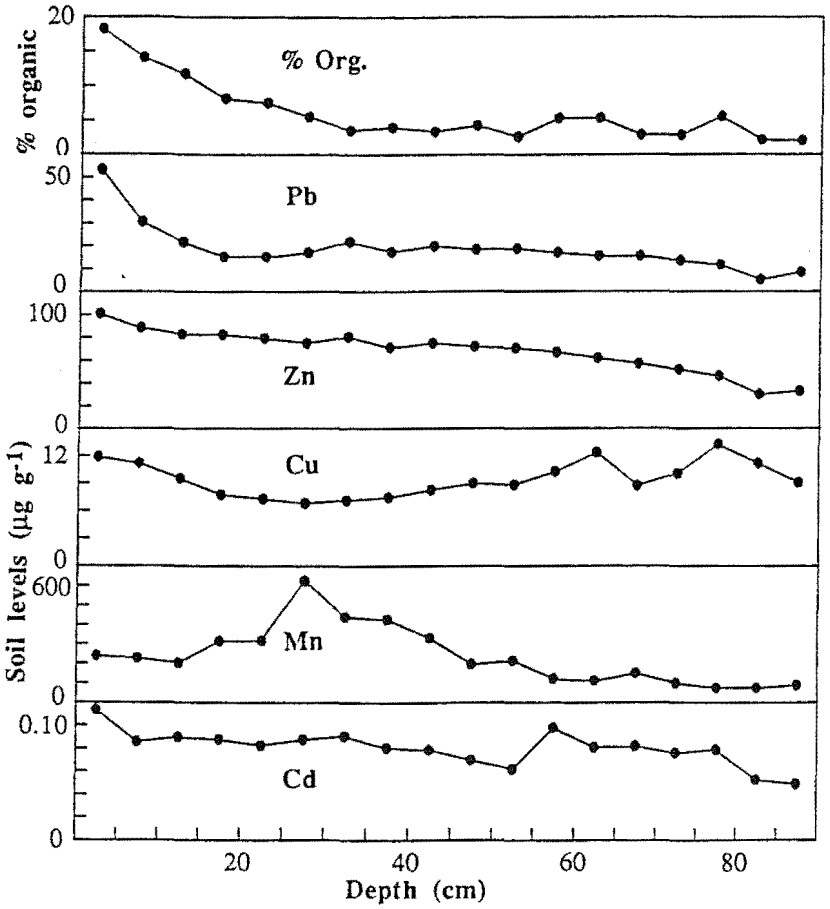

Figure 5.11 Depth profile of Riccarton Bush soil 4M HNO_3-extractable metal content

Table 5.1 4M HNO_3-extractable metal content of Canterbury Plains rural topsoils

Element	Concentration (µg/g)
Pb	14 ± 4
Zn	52 ± 11
Cu	7.9 ± 2.0
Mn	433 ± 79
Cd	0.12 ± 0.08

Figure 5.11 indicates that lead is elevated in Riccarton Bush topsoil at 50 µg/g compared with levels of around 12 - 20 µg/g in Canterbury plains rural topsoils. These

'background' levels are comparable to overseas estimates of the natural lead content of a variety of soils (Chow, 1973). Chow reports that soils close to heavy traffic can reach up to 3000 μg/g; thus the Riccarton Bush soil cannot be considered to be heavily contaminated with lead. The distribution of lead within the profile generally follows closely the distribution of the soil organic matter, the relationship being highly significant ($R=0.830$, $p<0.001$). Lead appears immobilised in the upper 10-15 cm with little evidence of transport down the profile.

Comparison of the data in Table 5.1 with Figure 5.11 shows that manganese and cadmium are not elevated above normal levels in Riccarton Bush topsoil. Zinc is enriched around twofold however, and copper shows very slight enrichment. A slow decrease in the zinc concentration down the profile may be due to its greater mobility in soil compared with lead.

The manganese profile exhibits a peak at 27 cm depth; this corresponds to a zone of ferromanganiferous concretions which were visible at this depth.

Thus, for total metal concentrations, lead and zinc are enriched over normal levels. However, a strong extracting agent such as 4M HNO_3 does not necessarily provide a useful indication of what is available to the plant. The literature on the choice of "plant-available" extractants is quite complex and contradictory. In general, weak ionic reagents such as 0.01M $CaCl_2$ indicate the composition of the soil solution, whereas chelating agents such as EDTA and DTPA are considered to indicate the total "pool" of metals that may be available to plants, especially organically-bound metals (Adriano, 1986). For copper, EDTA is considered to be a realistic extractant for estimating plant availability because it is believed that a copper-specific root exudate can remove copper from its organic complexes (Goodman et al., 1979). Thus, an extraction with 0.04M Na_2EDTA, adjusted to pH6 with NaOH, was carried out on the Riccarton Bush core.

The depth profiles of EDTA-extractable metals (Figure 5.12) are more strongly related to the distribution of organic matter than the 4M HNO_3-extractable metals are. This is not surprising, as EDTA is most likely to extract metals from their organic complexes. This difference may be seen by comparing the correlation coefficients given

in Table 5.2. The table shows that EDTA extractable lead, zinc, copper and cadmium are all highly significantly correlated with soil organic matter.

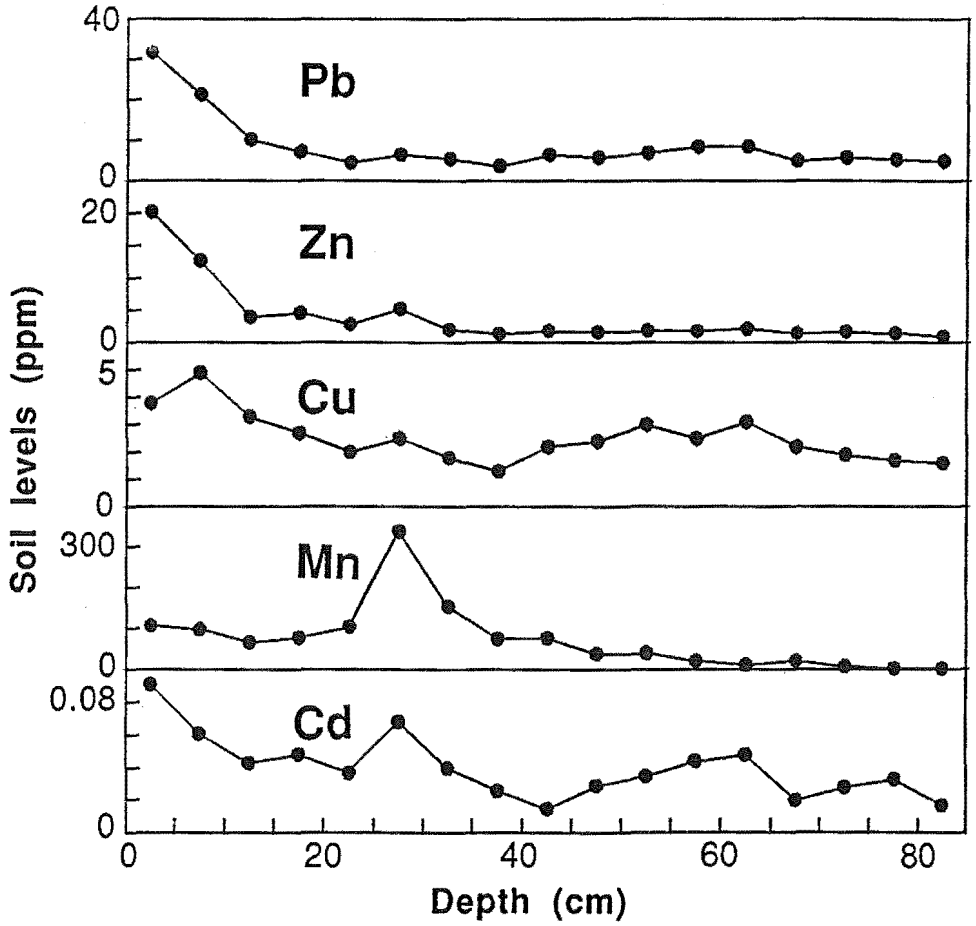

Figure 5.12 **Depth profile of Riccarton Bush soil 0.04M EDTA-extractable metal content**

Table 5.2 Correlations between soil organic matter, total metals and extractable metals in Riccarton Bush soil

Element	Total metals		Extractable metals	
	Significance* Correlation (R)	Metal-organic Level (N=18)	Significance* Correlation (R)	Metal-organic Level (N=17)
Pb	0.830	p<0.001	0.891	p<0.001
Zn	0.718	p<0.001	0.907	p<0.001
Cu	0.305	p>0.10	0.763	p<0.001
Mn	0.038	p>0.10	0.212	p>0.10
Cd	0.698	p<0.01	0.806	p<0.001

* $p < 0.001$ Highly significant
$p < 0.01$ Very significant
$p < 0.02$ Significant
$p < 0.05$ Just significant
$p > 0.05$ Not significant

In terms of metal pathways, it is unlikely that the slight enrichment of lead in Riccarton Bush topsoil could produce the observed accumulation of lead in the kahikatea ring wood because lead is strongly associated with the soil organic matter and hence effectively immobile. This conclusion is supported by studies which show that plant uptake of lead is not proportional to the lead content of the soil. Karamanos et al. (1976) found that increasing soil lead from 20 to 100 μg/g lead did not alter the dry-weight yield of lead in alfalfa grass. These and other authors have noted that plants appear to have a barrier to the transfer of lead across their roots.

Zinc, which is also slightly elevated in Riccarton Bush topsoil, is also strongly correlated with the organic fraction, but it is more likely that plants may be able to utilise organically-bound zinc as it is a plant micronutrient (Mortvedt et al., 1972). Hence, this pathway may have contributed to the zinc accumulation observed in the ring wood. Also, zinc is considered to be more mobile in the soil profile (Adriano, 1986).

The alternative entry route for metals transferred through the atmosphere into tree ring wood is via direct deposition of aerosol onto bark and foliage. Bark is well known as an efficient collector of airborne particles and has been used as an indicator of atmospheric metal concentrations (Tanaka and Ichikuni, 1982; Abergas et al., 1987). It is likely that the porous structure of bark acts as a trap for airborne particles too small to settle under gravity. Hall et al. (1975), in a mass-balance study of a woodland ecosystem, noted that the bark acts as a site for heavy metal accumulation.

Tree foliage may also be effective at intercepting aerosols; Schlesinger and Reiners (1974) found that artificial foliar collectors intercepted five times more lead deposition than conventional dustfall collectors. Interception is thought to be an important route for removal of the stable aerosol (<10 μm) whereas larger particles settle out quickly near their source (Pierson et al., 1973).

Although the Riccarton Bush topsoil is not highly enriched with lead, it has been found that near to a source, the concentration of lead in surface soils and vegetation shows a much more rapid decline with distance than do airborne concentrations (Daines et al., 1970).

To investigate sites of accumulation of heavy metals within Riccarton Bush, bark and foliage samples were analysed. The results (on a dry-weight basis) are presented in Tables 5.3 and 5.4. Also included in Tables 5.3 and 5.4 are enrichment factors (EFs) calculated relative to manganese which was assumed not to be influenced by location. In fact, manganese in the background bark sample was over twice the concentration of urban bark manganese, hence the EF values for urban bark are probably artificially high.

Table 5.3 Heavy metals in kahikatea bark from urban and background sites

Element	Urban (μg/g)*	Background (μg/g)*	EF**
Pb	43±6	0.31±0.08	330
Zn	58±12	11±3	14
Cu	12±3	5.0±1.3	5.7
Mn	73±19	170±59	1.0
Cd	0.91±0.11	0.021±0.009	100

* Mean of six samples ± standard deviation

** $EF = \frac{[M_{urban}] \times [Mn_{background}]}{[M_{background}] \times [Mn_{urban}]}$

Table 5.4 Heavy metals in kahikatea foliage from urban and background sites

Element	Urban (μg/g)*	Background (μg/g)*	EF**
Pb	41±9	3.0±0.9	15
Zn	23±6	11.6±1.2	2.3
Cu	6.2±2.1	4.2±0.9	1.7
Mn	85±9	97±11	1.0
Cd	0.15±0.04	0.20±0.05	8.5

It is clear that both bark and foliage are enriched with lead, zinc, copper and cadmium in urban kahikatea trees compared with background trees. The enrichment is most pronounced for lead and cadmium. A second point is that enrichments are higher for bark than for foliage; this is consistent with a study by Smith and Siccama (1981) which found metal enrichments for different tree parts to be in the order bark > foliage > wood. However, an alternative explanation for the lower foliage enrichments is that the foliage from the background trees has been contaminated by the collection method, as a shotgun was used to fell branches from the canopy. This would produce smaller ratios of urban to background concentrations.

In conclusion, analyses of soil cores and tree bark and foliage at both the urban and background sites suggest that the observed accumulation of lead and possibly cadmium in urban kahikatea ring wood is probably due to direct deposition of airborne particulate metals onto tree surfaces, rather then via soil enrichment and root uptake. Soil pathways are more likely for zinc and copper as they are plant micronutrients and have well-defined entry routes into plants.

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Chapter 6

Historical monitoring by peat analysis

6.1 INTRODUCTION

In the previous chapter, the use of tree rings as historical monitors was discussed. A complication with the use of this technique is that vascular, or rooted, plants receive nutrients from the soil as well as from the atmosphere (Glooschenko, 1986). In 1971, Goodman and Roberts found that mosses (which are nonvascular hence receive all nutrients from the atmosphere) could be used as indicators and integrators of aerial metal levels. The efficiency of mosses at collecting airborne particulates is thought to be due to their porous structure and high cation exchange capacity, even at low pH (Swaine and Godbeer, 1984).

Thus, it has been suggested that peat bogs, which are accumulations of mosses and other higher species, may retain a historical record of atmospheric metal deposition. Coleman (1985) and Glooschenko (1986) have recently reviewed the literature and both conclude that although some authors have reported successes (Livett et al ,1980; Madsen, 1981; Ruhling and Tyler, 1973), complex physicochemical processes in peat bogs are not well enough understood to make results unequivocal. In particular, the position of the water table can alter trace element distributions in peat bogs. Damman (1978) found that lead, zinc and manganese had been retained in well-drained peat, but had been mobilised and removed in the permanently anaerobic zone below the water table. In the zone of water table fluctuations, some elements accumulate, as in soils, and some are lost.

Another problem is the establishment of an accurate time scale within a peat profile. Radiocarbon dating has been widely used in the past, but is inaccurate for samples younger than 200 years before present. Contamination of older peat (by the leaching downward of younger material) can also be a problem. Dating by pollen analysis requires historical data relating to vegetation changes (Livett et al., 1979). Because of these limitations, dates obtained by two independent methods are preferable.

In this study, cores were collected from three peat bogs located in inland Canterbury. One bog was located on the summit of Arthurs Pass, one about 2 km south of the pass, and one in Broken River Basin, a much drier area 40 km to the south-east. The cores were dated by pollen analysis, with some cross-checking by ^{14}C dating, and the concentrations of lead, zinc, copper, manganese, cadmium and calcium measured. From the distributions of these elements within the cores it was hoped to gain an understanding of their chemical behaviour and movement within the peat profile.

A complication in this study was that the two Arthurs Pass bogs were found to be comprised of cushion bog species, rather than moss. Glooschenko (1986) has discussed the use of different species of bog vegetation in monitoring of atmospheric deposition, and concluded that the use of lower plants (mosses and lichens) is preferable because the root systems of higher plants may penetrate into underlying substrates.

These bogs can be considered to come from background locations with respect to major urban areas. However, the region is traversed by State Highway 73 which carries an average of 780 cars/day (National Roads Board, pers. comm.). A relevant study is that of Ward et al. (1973), who studied a low-volume highway (1200 cars/day) in the central North Island and found that elevated levels of lead in vegetation were detectable up to 100 m either side of the road, with a roughly exponential decline away from the road. Thus, State Highway 73 must be considered as a potential source of anthropogenic airborne metals to the peat bogs, two of which were located within 100 m of the road.

6.2 EXPERIMENTAL

6.2.1 Sampling sites

a) Main Divide Map reference NZMS 260 K33 924102. This sampling site was located in a wet bog formed behind a moraine on the summit of Arthurs Pass, Canterbury, 100 m west of State Highway 73. The bog consisted of fibrous, well-humified dark brown peat probably of around 2 m depth. The main peat-forming species were the bog cushions *Donatia novae-zelandia* and *Oreobolus pectinatus*.

b) Whites Bridge Map reference NZMS 260 K33 922080. This site was located on a fluvioglacial terrace 300 m south of Whites Bridge, Arthurs Pass, and 50 m southwest of State Highway 73. The peat was approximately 1.5 m deep and was of similar composition to the Main Divide bog.

c) Craigieburn Map reference NZMS 260 K34 069826. This site was located on a terrace of Cave Stream in Broken River basin, Canterbury, and approximately 400 m east of State Highway 73. The bog consisted of light brown, uncompressed, fibrous peat overlying alluvial gravels at 102 cm depth. The main peat-forming species was the moss *Sphagnum falcatulum*, with some sedge remains also present. Scattered charcoal fragments were found between the depths of 24 and 38 cm.

The general location of the three sites is shown in Figure 6.1.

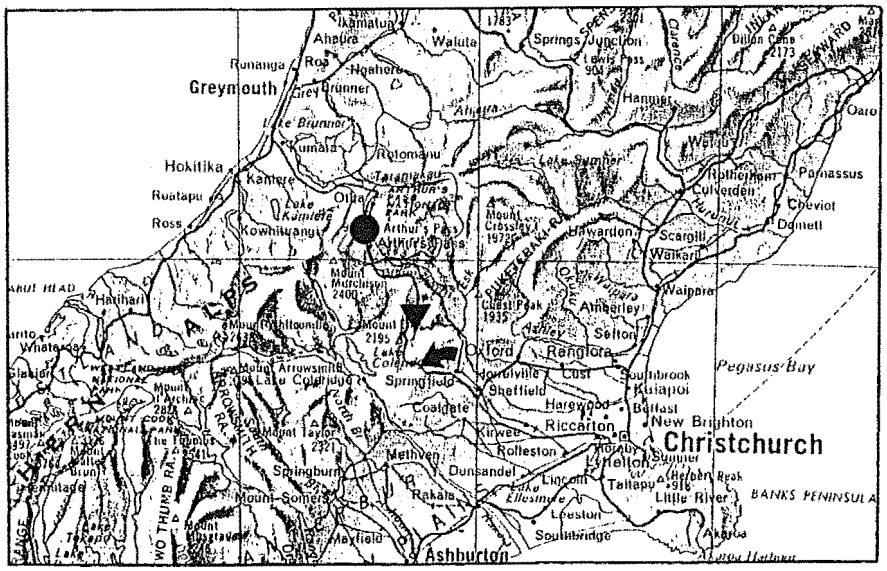

Figure 6.1 Map of central South Island showing locations of Main Divide and Whites Bridge sites (closed circle) and Craigieburn site (closed triangle). State Highway 73 is arrowed

6.2.2 Coring procedure

Monolithic cores were removed from the peat bogs by inserting PVC piping (15 cm internal diameter x 45 cm depth) into the bogs and slicing across the bottom edge with a stainless steel knife. Because of the fibrous nature of the peat, compression of the peat was found to be a problem if the corer was forced into the peat. To avoid compression, teeth were cut into the corer so it could slice through the peat. The core ends were immediately sealed with plastic film and the cores transported back to the laboratory in the pipes.

Once back in the laboratory, the cores were extruded from the pipes and cut into 2 cm sections with a stainless steel knife. Roots were removed with stainless steel tweezers to minimise contamination from younger material. For heavy metal analysis, subsamples were removed from the centre of each section (to avoid surface contamination from the corer) with an acid-washed glass spatula. Analytical samples were dried to constant weight in a clean oven at 50°C.

6.2.3 Field measurements

a) Water table The position of the water table was recorded at all sites, both at the time of coring and during a later visit to obtain E_h data.

b) pH Because of a shortage of material, a complete pH depth profile was obtained only for the Whites Bridge core. Five grams of field-moist peat were mechanically stirred with 12.5 ml 0.01M $CaCl_2$ and left to settle overnight. The pH of the supernatant solution was measured with a glass/calomel electrode couple. The pH of the groundwater was also determined for each bog, after removing a sample to the laboratory in a polypropylene bottle.

c) E_h When measuring the E_h of anaerobic environments, care must be taken to avoid contact with the atmosphere because of the effect of dioxygen (Hermann and Neumann-Mahlkau, 1985). In this study E_h was measured *in situ* by inserting the platinum probe to the required depth; the calomel electrode was placed in a KCl-soaked filter paper in contact with the surface of the peat. Each reading was taken after 4-5 minutes, the time necessary for a constant reading to be obtained.

6.2.4 Analytical procedures

Following the technique recommended by Livett et al. (1979) and Damman (1978), 5 ml of 4:1 concentrated HNO_3:$HClO_4$ (Aristar grades) were added to each dried subsample (0.7 - 1.0 g). This mixture was boiled gently in covered Pyrex beakers for 30 minutes and then filtered through acid-washed Whatman No. 540 filter paper into 25 mls.

Copper, lead and cadmium were analysed by graphite furnace AAS at 324.8 nm, 283.3 nm and 228.8 nm respectively. Matrix modification with H_3PO_4 was used to improve peak shape (Section 7.3.1). Zinc and manganese were analysed by flame AAS at 213.9 nm and 279.5 nm. The solutions were accurately diluted ten times to avoid the problem of the burner blocking up with salts.

Calcium measurements were made on a separate 5 ml subsample removed from each solution. To avoid interference by phosphates (due to the formation of refractory $Ca_3(PO_4)_2$) the hotter C_2H_2/N_2O flame was used. Since calcium is partially ionised at the higher temperatures, the addition of a more easily ionised metal is required. Potassium (2000 μg/g) was used as an ionisation suppressant and the calcium standards were matched to this ionic strength. Calcium absorbance was measured at a wavelength of 422.7 nm using a lamp current of 3 mA and a slit width of 0.2 nm.

The organic content of the peat was estimated by the percent weight loss after ignition. Accurately weighed 0.2 g samples were ashed to constant weight at 430°C.

6.3 RESULTS AND DISCUSSION

6.3.1 Redox potential, pH and organic content of peat profiles

The E_h depth profiles for each of the 3 sites are shown graphically in Figure 6.1 and the rainfall data for the sites are shown in Table 6.1.

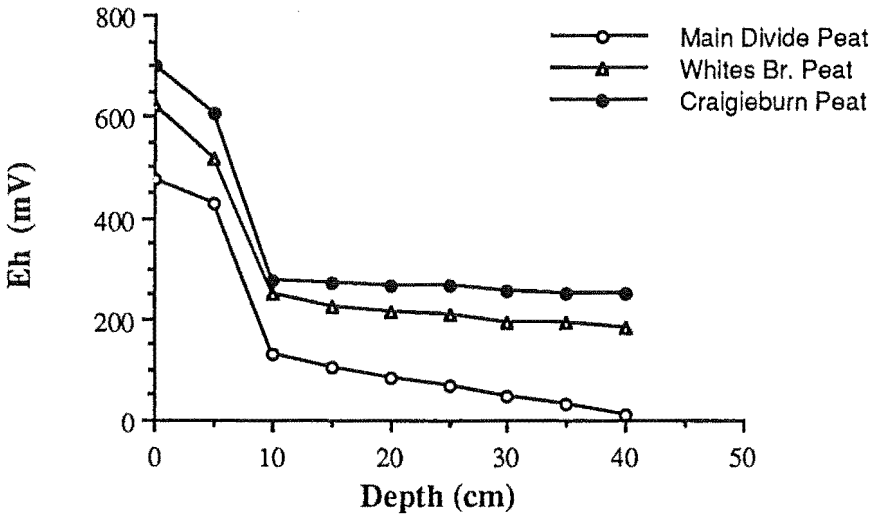

Figure 6.1 Depth profiles of redox potential for peat cores

Table 6.1 Annual rainfall at sampling sites

Site	Annual Rainfall (mm)	Distance from Main Divide(km)
Main Divide	4800	0
Whites Bridge	4400	2
Craigieburn	1600	40

The Main Divide bog has the most anaerobic conditions, which is probably due to the higher rainfall in the location and its poor drainage. The Whites Bridge bog, which receives slightly less rainfall, is a less reducing environment and this bog appeared to be better drained. The Craigieburn site was the least waterlogged, reflecting the lower rainfall.

The E_h profiles for all three sites show a marked change of slope at 10 cm depth. This change probably reflects a change in the drainage of the peat. The zone below 10 cm is likely to be permanently waterlogged, whereas above 10 cm, air may penetrate at times giving rise to more oxidising conditions.

The pH profile for Whites Bridge peat is shown in Figure 6.2. The upper part of the bog has acidic pH values of 3.6 to 4.0, which decrease slightly to 3.4 - 3.6 below 10 cm depth. The high acidity in peat is most likely due to organic acids released by humification of plant remains. Hemond (1980) found that dissociation of weak organic acids could quantitatively account for the observed pH of 3.8 in a Massachusetts bog.

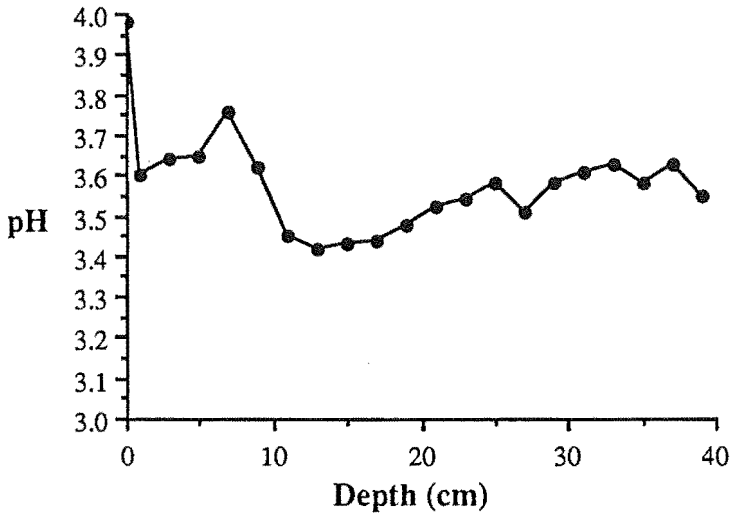

Figure 6.2 Depth profile of pH in Whites Bridge peat

The estimated organic content of the Whites Bridge profile is shown in Figure 6.3. Peat has a much higher organic content than mineral soils, and decreases only slowly down the profile, in this case from 95% at the surface to 85% at 40 cm depth. It is thought that the high acidity of the peat inhibits bacterial decomposition of organic matter (Glooschenko, 1986). Macroscopic plant remains were still visible at the bottom of the cores collected in this study.

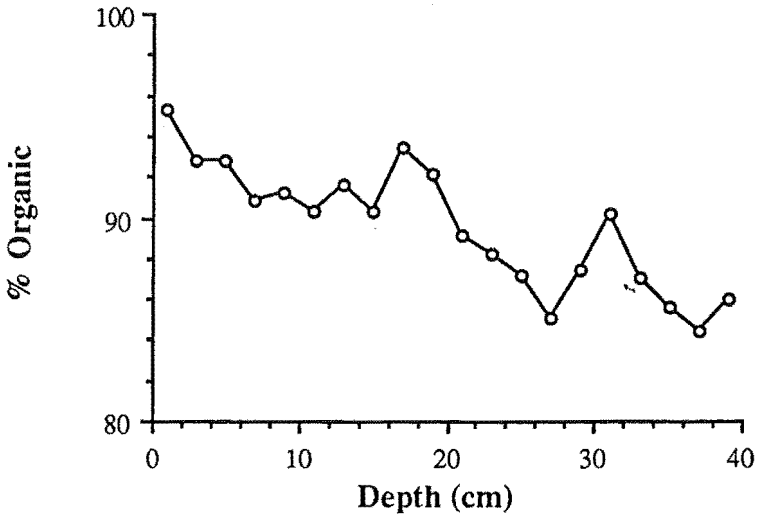

Figure 6.3 Depth profile of organic content in Whites Bridge peat

6.3.2 Total metal distributions

Results of the total metal analyses are listed in full in the Appendix. Depth profiles for total metal concentrations, expressed on a dry-weight basis, are shown

graphically in Figures 6.4, 6.5, and 6.6. It should be noted that the analytical errors in these results are approximately 10% for lead, copper and cadmium; and 5% for zinc, manganese and calcium. These errors arise mainly from instrumental precision limits. The error involved in subsampling each core were found to be approximately 15%; this was evaluated by analysing six subsamples from a single segment of peat. Because only one core was obtained from each site, the magnitude of the sampling error is unknown, but is likely to be >15%.

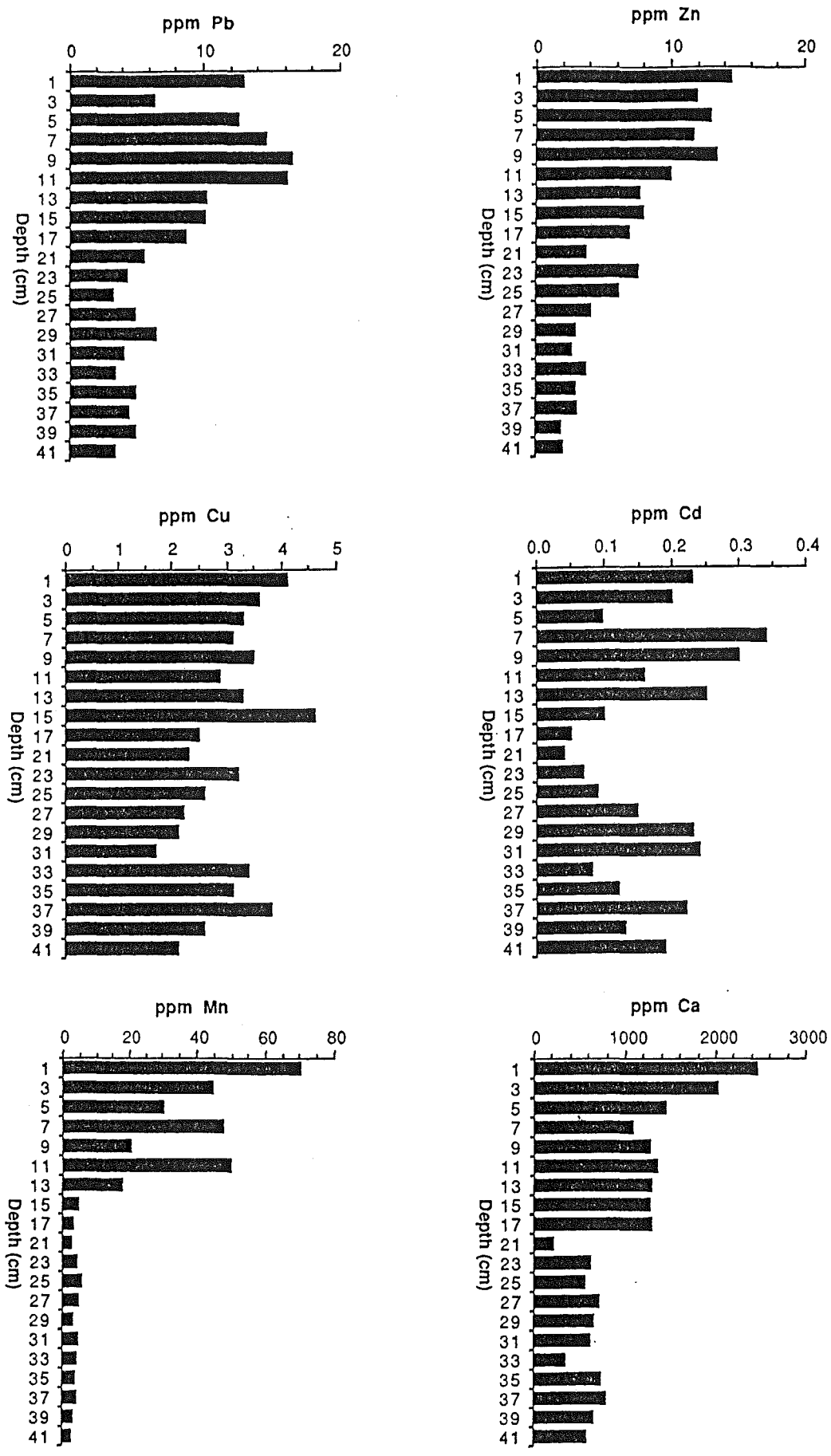

Figure 6.4 Concentrations of Pb, Zn Cu, Mn, Cd and Ca in Main Divide peat

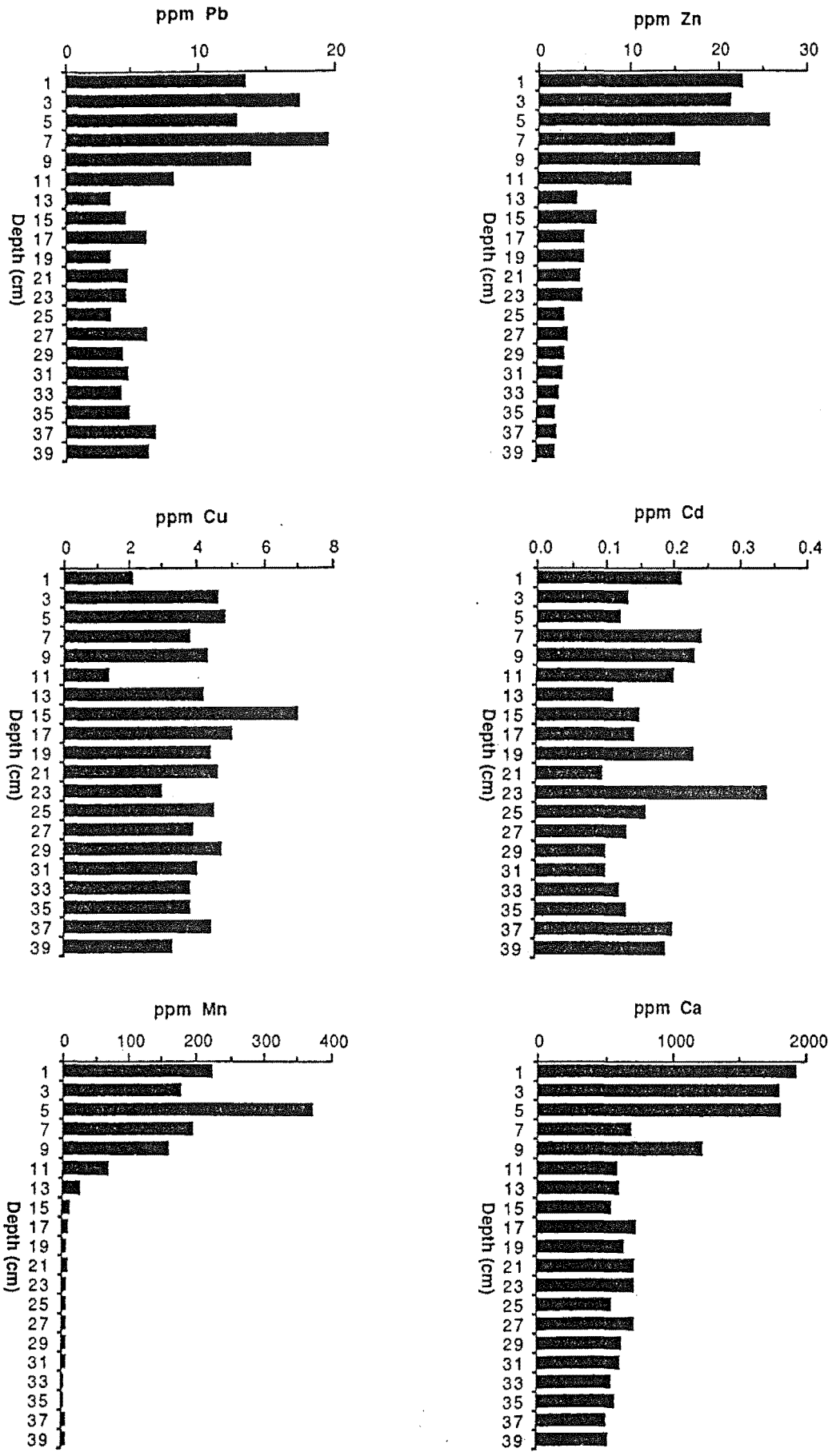

Figure 6.5 Concentrations of Pb, Zn Cu, Mn, Cd and Ca in Whites Bridge peat

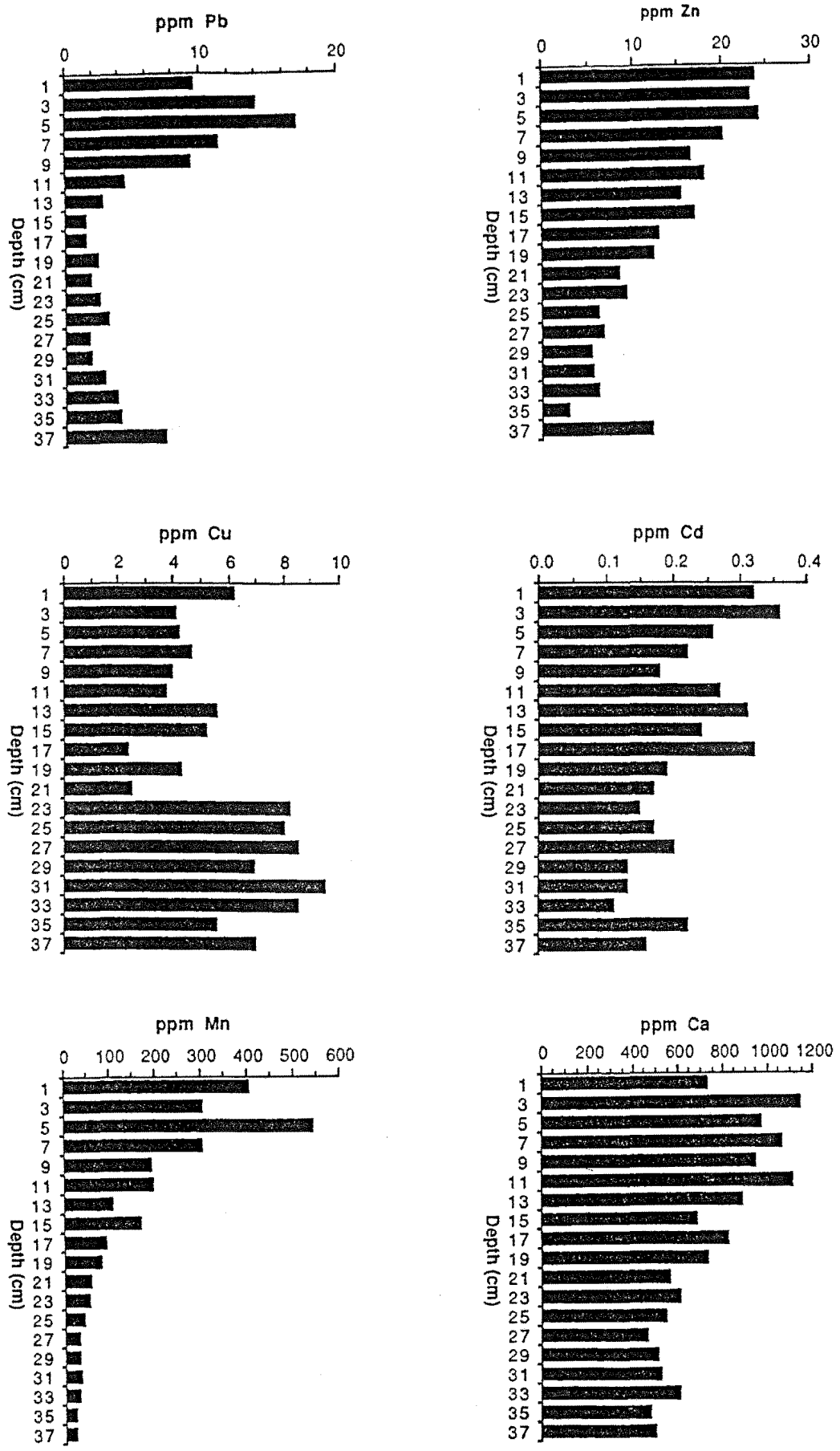

Figure 6.6 Concentrations of Pb, Zn Cu, Mn, Cd and Ca in Craigieburn peat

a) Lead Lead profiles from the three sites are very similar, despite differences between the sites in rainfall and redox conditions. In each case, levels fall from 10-15 μg/g lead above about 10 cm depth to 4-5 μg/g below this depth. Thus, lead appears to have been partially removed from the permanently anaerobic peat. A similar trend was also observed by Damman (1978).

Results from the previous section showed that anaerobic peat is characterised by a very high organic content and low pH and E_h, which influence metal speciation. In a reducing environment containing sulphur species, one could predict from an E_h/pH stability field diagram (e.g. Garrels and Christ, 1965) that lead(II) would be immobilised as PbS because of the very low solubility of this compound($K_{sp} = 8.4 \times 10^{-28}$ at 25°C). Since lead does not appear to be retained in the anaerobic peat, it could be concluded that either the sulphide concentration is insufficient to form PbS, or other species are more important. Microanalyses for sulphur content were performed on samples from the Whites Bridge Bog (32-34 cm depth) and the Main divide Bog (24-26 cm depth). In both cases the sulphur content was approximately 800 μg g^{-1} , on a dry-weight basis. However, nothing is known about the speciation of the sulphur.

It might be assumed that the very high organic content of the peat would significantly influence metal speciation, since metal-organic complexes, especially for lead and copper, are important in most soils (Adriano, 1986). However, the low pH of the peat should disfavour these complexes. Data reported by Gregor et al. (1988) indicates that for a Cu^{II}-fulvic acid system, at pH 3, almost 100% of the copper exists as the free metal ion whereas at pH 5, around 10-20% free Cu^{2+} remains. However, in natural systems, kinetic factors may often mean that reactions are slow hence thermodynamically unstable species can exist for long periods. Jones (1987) has reported that 20-30% of the lead (in a British blanket peat) was associated with organic matter.

It is likely that lead will be associated with the iron(III)-manganese(IV) oxide fraction and Jones (1987) found that about half the lead was associated with this fraction. Since Fe/Mn oxides are solubilised under reducing conditions by reduction to Fe(II) and Mn(II), the depletion of lead in the anaerobic peat can be explained as the release of lead from the oxidised Fe/Mn oxide fraction. The strong positive correlation between lead and

manganese for all the profiles, shown in Table 6.2, supports this explanation. Correlations between lead and E_h for all three sites are shown in Table 6.3. These data show that the lead concentration is strongly related to E_h in the Craigieburn and Whites Bridge bogs but less strongly related in the Main Divide peat.

Table 6.2 Correlations between Mn and other metals in the peat profiles

Element	Main Divide (N=20)		Whites Bridge (N=20)		Craigieburn (N=19)	
	r	Significance*	r	Significance	r	Significance
Pb	0.708	p<0.001	0.821	p<0.001	0.846	p<0.001
Zn	0.819	p<0.001	0.957	p<0.001	0.900	p<0.001
Cu	0.416	p>0.05	0.109	p>0.1	0.414	p>0.05
Ca	0.820	p<0.001	0.851	p<0.001	0.703	p<0.001
Cd	0.451	p<0.05	0.089	p>0.1	0.596	p>0.1

* p<0.001 Highly significant
p<0.01 Very significant
p<0.02 Significant
p<0.05 Just significant
p>0.05 Not significant

Table 6.3 Correlations between Pb and E_h in the peat profiles

Site	Correlation (N=9)	
	r	Significance
Main Divide	0.677	p<0.05
Whites Bridge	0.894	p<0.01
Craigieburn	0.941	p<0.001

It is not clear whether or not lead is retained in surface peat. Hemond (1980) carried out mass balance measurements on a Massachusetts bog and calculated the atmospheric input of lead to be 54 mg/m^2/yr. Since only 1 mg/m^2/yr was found to be lost from the bog, a high proportion of lead is retained. The annual rainfall at the Massachusetts site was 1.45 m, which is slightly lower than at the Craigieburn site. However, in this study, surface lead concentrations do not appear to depend upon rainfall, and hence the results of Hemond's study are probably applicable to this one.

Another question is whether the surface peat contains elevated lead levels due to the proximity of the Arthurs Pass bogs to the main highway. The surface lead concentrations found in this study (around 10-15 μg/g) are similar to reported overseas data from background sites (Livett et al., 1979; Damman, 1978). This similarity suggests that peat lead levels are probably not elevated.

Calculation of enrichment factors is another possible approach to this question. The lead:calcium ratios in the upper part of the peat were normalised by dividing by the ratio of lead to calcium in typical uncontaminated vegetation using the expression* $EF_{plant} = (Pb_{peat}/Ca_{peat})x(Ca_{plant}/Pb_{plant})$. The lead and calcium concentrations in the ring wood of the Wanganui River Flats kahikatea trees (discussed in Chapter 5) were taken as being typical of natural vegetation. The enrichment factors are presented in Table 6.4.

Table 6.4 Enrichment factors for upper part of peat cores

Depth (cm)	EF_{plant}* Main Divide	Whites Bridge	Craigieburn
0-2	118	158	295
2-4	72	219	277
4-6	196	159	396
6-8	306	194	227
8-10	295	257	223

The data listed in Table 6.4 show that lead is enriched over calcium in surface peat relative to other vegetation. However, this is probably not due to anthropogenic input, but to the greater affinity of the peat humic substances for lead (Kabata-Pendias and Pendias, 1984). This interpretation is supported by the fact that the EF values do not show a maximum in the top 2 cm of the peat, which is the most recently formed. However, the extent of redistribution of lead in the peat is not known. It can be concluded that any anthropogenic lead originating from motor vehicle exhausts is undetectable in the surface peat cores measured.

b) Zinc The depth profiles for zinc have a similar pattern to those for lead. Zinc levels seem to show slightly greater proportional reductions than lead below the water table. This may be because zinc is more strongly associated with the Fe/Mn oxide fraction, as shown by the higher correlation coefficients between zinc and manganese given in Table 6.2. Jones (1987) also found that zinc and lead showed very similar chemical partitioning in peat.

c) Copper The copper profiles differ from those of lead and zinc as copper hardly varies down the profile. This is probably due to an association between copper and the organic fraction of peat, regardless of the low pH discussed previously. For the

Whites Bridge profile, the copper and organic content do not show any correlation (r=0.000, N=20 pairs) but this is not surprising considering the high organic content of the peat compared with the low concentration of copper. Only a small proportion of the available complexing sites will be occupied by copper (McLaren, pers. comm.). The affinity of copper for organic matter is well-documented (e.g. Davies, 1980). Jones (1987) found that most copper was indeed organically-bound and hence relatively immobile within the profile. Coleman et al. (1956) measured stability constants for Cu(II)-peat complexes and concluded that most Cu(II) in peat will exist in this form.

d) Manganese Manganese distributions within the profiles show a strong relationship to the redox status of the soil. Manganese appears to be removed from the zone below the permanent water table, which is consistent with the formation of soluble Mn^{2+} from insoluble MnO_2 as the E_h drops. The low pH assists in keeping the Mn^{2+} in solution.

In the surface peat, the highest manganese concentrations (400-600 μg/g) occur at the Craigieburn site, which is also the least reducing, and the lowest manganese concentrations are in the Main Divide peat which is the most reducing. Hence, manganese retention appears to be strongly controlled by the redox conditions.

e) Cadmium The cadmium depth profiles show no distinctive trends and are similar to the copper profiles. The immobility of cadmium in the peat profile is surprising as cadmium is usually relatively mobile in soils because the free ion (Cd^{2+}) is favoured under a wide range of pH and E_h conditions. An obvious explanation would be that the speciation of cadmium is similar to that for copper, that is, associated with organic matter. Gong et al. (1977) studied the associations of cadmium in several environmental matrices and found that cadmium is organically-bound. These authors noted that cadmium is enriched in soils relative to sediments as the former have a higher organic content (typically 20-25% in soils compared to 5-10% in sediments). To extend this argument would suggest that peat would be further enriched in cadmium relative to soils. This trend was indeed observed in this study. Peat cadmium concentrations are 0.1 to 0.3 μg/g compared to levels of 0.05 to 0.1 μg/g in Canterbury Plains soils (data discussed in Chapter 4).

f) Calcium The calcium depth profiles found in this study are similar to those reported by Damman (1978) and and show a slow decrease downwards. The data in Table 6.2 shows that the calcium distribution is strongly related to the manganese distribution, but this may be coincidental.

6.3.3 Chronology of peat cores

Pollen analyses were carried out on each core (P. Randall, pers. comm) and several samples were submitted to the Institute of Nuclear Sciences, DSIR, Wellington, for ^{14}C dating. Results are summarised in Table 6.5, and where comparisons are possible, reasonable agreement exists between the two methods.

Table 6.5 Chronological data for peat cores

Site	Depth (cm)	Age (years B.P)	Technique	Peat Accumulation Rate
Main Divide	40	180	Pollen	1 cm / 4.5 years
	42	<200*	^{14}C	1 cm / <4.8 years
Whites Bridge	42	500	Pollen	1 cm / 11.9 years
	42	496±61	^{14}C	1 cm / 11.8 years
Craigieburn	36	120	Pollen	1 cm / 3.3 years

* Limit of detection for ^{14}C dating analysis

It is not known why the three sites have had different rates of peat accumulation. In particular, the difference in growth rates between the Main Divide and Whites Bridge bogs is surprising, as these bogs are comprised of the same species, are at a very similar altitude, and receive very similar rainfall. Compared with the data reported by Livett et al. (1979), the accumulation rates are fast, with a range of 1 cm in 5.5 years to 1 cm in 20 years considered to be the normal range. These authors report that in general, the growth rate of a bog slows down as the degree of humification increases. It is thought that as the peat becomes denser and more impermeable to ground water, the growing surface of the bog becomes cut off from the groundwater and must receive all its nutrients from atmospheric input.

A possible explanation for the difference observed in growth rates is that the faster-growing bogs are not purely ombrotrophic (nourished by rainfall) but also receive

nutrients from the mineral substrate (minerotrophic). Another possibility is that the dates from which the accumulation rates are derived are erroneous.

6.3.4 Calculation of metal deposition rates

Given the uncertainty in both knowledge of behaviour of metals in peat and establishment of an accurate chronology, it would seem very risky to assign deposition rates with any degree of certainty. However, by making the following assumptions deposition rates can be calculated.

a) Assume the dates determined by the ^{14}C and pollen techniques to be accurate.
b) Assume a uniform growth rate (and uniform compaction) throughout the peat.
c) Assume that metals are retained in the surface 10 cm of the peat .
d) Assume a factor of 11.3 (calculated from available data) to exist between the subsample used for analysis of metal content and the entire section 2 cm deep by 0.0177 m^2 in surface area.

Thus, the mass of each metal down to 10 cm depth was calculated, multiplied by 11.3 to express on a surface area basis, and finally converted to units of $\mu g/m^2/day$. The results are displayed in Table 6.6, together with results obtained from a dustfall collector (see Chapter 3) located in Castle Hill basin,approximately 50 km south of Arthurs Pass.

Table 6.6 Metal deposition rates estimated from peat bogs

Element	Peat deposition rate ($\mu g/m^2/day$)			Deposition Gauge ($\mu g/m^2/day$)
	Main Divide	Whites Bridge	Craigieburn	Castle Hill
Pb	2.7	1.4	2.4	1.8 ± 0.2
Zn	2.8	1.8	4.3	1.8 ± 2.0
Cu	0.78	0.34	0.93	0.83 ± 0.43
Mn	9.4	19.2	69	21 ± 11
Cd	0.049	0.018	0.052	0.0064 ± 0.0007
Ca	366	135	190	-

Several interesting points arise from the data presented in Table 6.6. Firstly, it is clear that metal deposition rates (with the exception of cadmium) calculated from peat bogs agree both with each other and with rates measured by a conventional fallout

collector placed at a similarly remote site to within a factor of 2 to 3. This agreement is very good considering the assumptions made in calculating the deposition rates from metal concentrations in peat.

Another point is that for all the elements except manganese, deposition rates are higher in the Main Divide and Craigieburn bogs than in the Whites Bridge bog. A possible explanation for this is that these faster-growing bogs receive additional nonatmospheric input from the underlying mineral substrate. It is also noticeable that the deposition rates obtained from the Main Divide and Craigieburn bogs tend to be higher than the rates measured with fallout collectors, which suggests an additional source of metals.

Manganese is an exception, as the concentrations of manganese in surface peat were found to be strongly related to redox conditions.

Another point is that for cadmium, peat deposition rates overestimate those obtained from the fallout collector for all the bogs, by factors of between 3 and 8. A possible explanation is that cadmium is concentrated by the humic substances in peat.

6.4 CONCLUSION

In this study, the distributions (between 0 and 40 cm depth) of lead, zinc, copper, manganese, cadmium and calcium in three peat bogs were studied. For the metals lead, zinc, manganese and calcium, the distributions appear to be strongly dependent upon the position and fluctuation of the water table, with concentrations being depleted in the permanently waterlogged zone. The most probable explanation is that in the severely anaerobic conditions prevailing below the water table, Fe^{III}/Mn^{IV} oxides (and associated metals) become solubilised by reduction to the Fe^{II} and Mn^{II} forms. However, the distributions of copper and cadmium were found to vary little with increasing depth and it is likely that these metals are predominantly organically-bound.

Thus, in terms of the potential of peat bogs for historical monitoring purposes, it seems unlikely that concentration profiles of lead, zinc, calcium or manganese will bear any relationship to the external supply of these elements, as their depth profiles in peat appear to be modified by internal factors. However, copper and cadmium appear to be

relatively immobile within the peat profile and it is more likely that analyses of concentration trends of these metals may be of use in reconstructing pollution histories.

In the surface 10 cm of the peat bogs, conditions were found to be less anaerobic and it is more probable that metals will be retained in the peat. Reported evidence (Damman, 1978; Hemond, 1980) suggests that metals are retained above the water table, and deposition rates calculated from metal concentrations in the upper 10 cm of the bogs showed good agreement with those measured by a conventional precipitation collector in a similar location. However, a complication that became evident was that the peat bogs may also be receiving additional nonatmospheric sources of trace metals.

A final comment is that in this study, no attempt was made to address the question of the natural variability of metal distributions in different parts of a bog. It would be necessary to evaluate this variability before drawing conclusions based on a single sample.

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Chapter 7

General experimental methods

In the previous chapters, experimental methods relevant to each section have been included with each chapter. However, general experimental methods will be discussed in this chapter, with emphasis on the technique of atomic absorption spectrophotometry which was used widely throughout this study.

7.1 GENERAL ANALYTICAL PROCEDURES

7.1.1 Volumetric equipment

All pipettes (including micropipettes) used in quantitative work were calibrated by dispensing and weighing aliquots of water. The calibration of pipettes was checked at frequent intervals throughout this study.

The volumetric flasks used in this study were B grade borosilicate glass, and were assumed to have errors in total volume as given by Vogel (1961). Nalgene polyethylene bottles were used for containing rainwater samples.

7.1.2 Cleaning procedures

Patterson and Settle (1976) report a sophisticated and thorough 21-day cleaning procedure for Teflon ware, which involves leaching with hot, concentrated HNO_3: HCl. However, most workers use an abbreviated and less severe version of this procedure. In this study, all containers were initially soaked in a non-ionic detergent made up with distilled water, then rinsed thoroughly with double-distilled water. The vessels were then soaked in hot 2M HNO_3 and left for two days, then rinsed very thoroughly with double-

distilled water. The final rinses were with Milli-Q water. Containers were dried under an infra-red heat lamp in a laminar-flow work cabinet in the Clean Room to prevent airborne contamination. Care was taken to prevent subsequent airborne contamination of the clean laboratory ware by storing beakers sealed in polythene bags, and ensuring that volumetric flasks were kept stoppered.

It is also most important to ensure that stoppers and lids are included in the cleaning procedures.

7.1.3 Reagents

a) Water High-purity water was made by passing single-distilled water through a continuously circulating Milli-Q water purification system, incorporating an activated charcoal cartridge and two mixed-bed ion-exchange cartridges. Water was drawn off when required through a 0.22 μm membrane filter. A conductivity meter placed after the ion-exchangers was used to check the performance of the system, with a resistance of 18 MΩ considered desirable.

The water obtained by this process was found to be of very high quality. Even when concentrated by a factor of 25 (by freeze-drying), the analytical signal from a sample of Milli-Q water was below the detection limit of graphite furnace AAS. This corresponds to levels of less than around 0.01 ng ml^{-1} for the metals studied.

Water was also purified in an all-glass still. Single, double and triple-distilled water was available. Because even the triple-distilled water was found to contain higher concentration of the metals of interest, Milli-Q water was the preferred reagent for analyses of samples containing ultratrace (sub-μg/g) concentrations of metals.

b) HNO_3 The nitric acid used for dissolution of samples in this study was BDH 'Aristar' grade, which was found to contain acceptably low levels of lead, zinc, copper, manganese and cadmium. However, BDH 'Analar' grade contained slightly higher levels of all the metals, and its use was avoided for dissolution of samples containing low levels of analyte metals. It was mainly used for cleaning purposes.

7.1.4 Standard metal solutions

a) Standard metal solutions Stock solutions (1000 μg ml^{-1}) of lead, zinc, copper, manganese, cadmium and calcium ions were prepared by dissolving the

calculated amount of Analar-grade metal salt in double-distilled water, and making up to a final volume of 1 litre. The solutions were made 1 mol l^{-1} in HNO_3 to stabilise the metal ions in solution. The salts used were $Pb(NO_3)_2$; $ZnSO_4.7H_2O$; $CuSO_4.5H_2O$; $MnSO_4.4H_2O$; $3CdSO_4.8H_2O$ and $Ca(NO_3)_2$. From these stock solutions, working solutions were prepared by dilution with Milli-Q water.

b) Buffers To calibrate the pH response of the glass/calomel electrode couple, the buffers used were 0.05M potassium hydrogen phthalate (pH 4.008 at 25°C), and 0.025M disodium hydrogen phosphate / 0.025 M potassium dihydrogen phosphate (pH 6.865 at 25°C). Each buffer was prepared by dissolving the calculated weight of pure, dry solid in 1 litre of double distilled water.

c) ZoBells solution To standardise E_h measurements using a platinum/calomel electrode combination, ZoBells solution, which contains a known and stable redox couple, is recommended (Nordstrom, 1977). This solution has a temperature-dependent potential given by the equation $E_{h\,ZoBell}$ (V) = 0.430 - 2.57 x10^{-3} (t - 25). ZoBells solution consists of 0.0033M $K_4Fe^{II}(CN)_6$ and 0.0033M $K_3Fe^{III}(CN)_6$ in 0.1M KCl, and was prepared by dissolving the calculated amounts of pure, dry solids in double-distilled water.

7.2 CONTAMINATION CONTROL

7.2.1 The analytical blank

Many authors (e.g. Patterson and Settle, 1976; Ahlers and Hunter, 1986; Mitchell, 1973) have argued that accurate, precise analytical results cannot be obtained unless the analytical blank is controlled and reduced as far as possible. The limit of detection (D.L.) of an analyte is directly related to the blank by the expression D.L. = x + kσ, where x is the mean value of the blank, σ is the standard deviation of the blank and k is usually assigned a value of 3 (Zief and Mitchell, 1976). Equivalently, the limit of detection is the lowest concentration which is statistically different to the blank (Keith, 1983). Thus, it can be seen that the threshold below which determinations are impossible is mainly established by the reproducibility of the blank.

It is important to recognise that contamination can arise at all stages of the analytical procedure, from sampling through to instrumental analysis, and the approach taken in this work was to run blanks for each part of the total analytical process to identify and minimise sources of contamination. The four principal sources contributing to the total analytical blank are the environment the analysis is performed in, the reagents used, the apparatus, and the analyst performing the analysis.The steps taken to minimise the blank contribution will be described for each phase of the total analytical process.

7.2.2 Sampling

When obtaining field samples, it is important to ensure that the analyst and sampling equipment are not sources of contamination to the sample. Probably the first workers to draw attention to the need for strict contamination control during sample collection were Murozumi, Chow and Patterson (1969) who provided an exhaustive account of the precautions taken to avoid contamination of Greenland and Antarctic ice and snow samples. Further papers by Patterson and coworkers continue this approach (e.g. Patterson and Settle, 1976; Elias et al., 1976; Shirahata et al., 1980; Ng and Patterson, 1981; Boutron and Patterson, 1983). The main features of the sampling procedures detailed in these papers are the thorough cleaning of all equipment and the need for the analyst to avoid contacting the sample.

In this work, the sampling equipment consisted of stainless steel soil corers; a stainless steel tree corer; a PVC peat corer and PVC precipitation collectors. The PVC items were soaked in 2M HNO_3 for several days then rinsed thoroughly with double-distilled water with a final rinse of Milli-Q deionised distilled water. The stainless steel corers were rinsed in Analar-grade acetone to remove grease; soaked for a few minutes in 1M HNO_3, then rinsed thoroughly with Milli-Q water. The corers were dried in the Clean Room under an infrared heat lamp, then stored in polyethylene bags to avoid subsequent airborne contamination.

Care was taken never to touch samples with the bare hands, as skin is well known to be a source of contamination (Murphy. 1976; Zief and Mitchell, 1976). Clean polyethylene disposable gloves were worn at all times. Once samples were obtained, they

were immediately sealed inside two polyethylene bags and labelled before transport back to the laboratory.

7.2.3 Sample handling

This stage covers all the steps involved in transforming the field samples into forms suitable for instrumental analysis.

The influence of the laboratory environment becomes important in handling samples. The air in an open laboratory has been shown to contain large numbers of particles (Patterson and Settle, 1976; Murphy, 1976; Zief and Mitchell, 1976). The concept of regulating laboratory environments has been very important in the control of analytical blanks. In 1966, U.S. Federal Standard 209a was established to monitor the concentration of particles in the air of work areas. Classes of clean environments are defined by the maximum number of particles 0.5 and 5.0 μm in diameter per cubic foot of air. For Class 100 air (the cleanest environment specified), the number of particles larger than 0.5 μm must not exceed 100.

The major development for providing particle-free air has been the high efficiency particulate air (HEPA) filter, which has an efficiency of 99.97% for the removal of 0.3 μm and larger particles. HEPA filters are routinely used for supplying Class 100 air.

Clean Room facilities were available during this study. The Clean Room consisted of a single room through which air is circulated, through two ceiling-mounted HEPA filters, at the rate of one room volume every 3 minutes. A change room, between the Clean room and the corridor, was used to store protective clothing consisting of lint-free nylon coats, cellulose caps and overboots. Two pairs of polyethylene disposable gloves were also used.

Laminar-flow work benches, rated to Class 100, were used for sample handling. A flow of HEPA-filtered air towards the analyst ensures that if care is taken to keep downstream from the sample, the contamination arising from particles of skin, hair, clothing, sweat and so on, should be minimised.

Some procedures had to be performed outside the Clean Room. There were no facilities in the room for ashing or digestion. For acid digestions, a perspex dust hood was constructed so that air would flow in through an acid-washed glass-fibre filter, and

out through a small vent in the top. The hood was placed over the digestion beakers and ceramic-topped hot plate and was found to be an effective way of reducing the airborne contamination at this stage.

Dry-ashing was carried out in a muffle furnace, which had a ceramic lining. To prevent particles from the lining falling into the sample containers, clean Pyrex dishes were inverted over the samples, leaving enough air space to allow an adequate air supply for ashing the samples.

It was also decided not to dry soil and peat samples in the Clean Room, because of the danger of contributing particles to the air stream. For the purpose of air-drying soil and peat, a dry glove-box was modified for clean work by coating the inside with lead-free paint, and passing air in through acid-washed glass-fibre filters. Samples and equipment were introduced through an airlock. Once the samples were dry, they were crushed between polyethylene sheets with a stainless steel rolling pin.

Filtrations are a step prone to contamination, both from the filter paper itself and from airborne contamination. The cellulose Whatman filter papers used for filter soil and peat were leached with 2M HNO_3 before use. Due to lack of space in the Clean Room, the filtrations were performed in the open laboratory. The apparatus was sealed with plastic film, and this was found to be an effective method of preventing airborne contamination.

7.2.4 Analysis

Once samples are in the volumetric flasks, further contact with the atmosphere is unlikely. However, it was found that during graphite furnace AAS determinations, the instrumental blank signal was reduced by keeping the door of the instrument room closed, presumably reducing dust circulation. It was also necessary to wear polyethylene gloves to prevent inadvertent contact of the skin with either the syringe or the sample solutions. The disposable Teflon syringe tip was acid-washed and rinsed in Milli-Q water between each injection.

As mentioned previously, the levels of metals in the reagent acids and water must be carefully determined by running blanks. If available commercial acids contain unacceptably high concentrations of the metals to be analysed, it will be necessary to

purify the acids by sub-boiling or iospiestic distillation (Zief and Mitchell, 1976 Mitchell, 1973). In this work, this was not found to be necessary. A careful assessment was made of contamination from glassware. If these precautions are followed, the detection limit of the analytical process may approach the instrumental detection limit.

7.3 INSTRUMENTAL ANALYSIS

7.3.1 Atomic absorption spectrophotometry (AAS)

a) Principles of AAS The basic principle of AAS is straightforward. The sample to be measured is converted to an atomic vapour, either by heating in a flame or in an electrically-heated furnace. A beam of monochromatic light from a hollow cathode lamp, corresponding to an allowable ground state to excited state transition for the analyte element, is passed through the sample. This beam will be partially absorbed by the ground state analyte atoms and its radiant power will decrease. The radiant power of the beam is is measured with a photomultiplier tube and amplifier, first with and then without the sample vapour in the optical beam; the decrease in power is proportional to the number of absorbing atoms in the beam. Empirical calibration curves are constructed from known amounts of the analyte, and the concentration of the analyte in the solution calculated.

In this study, both flame and graphite furnace AAS were used extensively, and will be discussed separately.

b) Flame AAS In 1955, Walsh first proposed the technique of flame AAS and since then, it has become the most widely used technique for the determination of the metallic elements. The technique involves spraying the sample in a fine mist into a hot air-acetylene or nitrous oxide-acetylene flame, where thermal decomposition generates a population of atoms. The principles of the instrumental systems currently in use are virtually unchanged from those proposed by Walsh, although recent innovations include faster electronics; electrodeless discharge lamps as well as hollow cathode lamps as monochromatic light sources, and the use of the hotter nitrous oxide-acetylene flame to determine the more refractory metals.

Interferences in flame AAS are well-documented and can be classified as spectral or chemical. Spectral interferences refer to interferences with the spectral line of the

analyte. Rarely, because the emission lines are so narrow, direct atomic spectral line overlap may occur. A more common form of spectral interference, encountered in the present work, is nonatomic absorption due to the matrix in which the analyte occurs. This is also known as background or nonspecific absorption and refers to absorption over a broad band of frequencies that may extend over the absorbance line of the analyte and thus cause positive interference. Broadband absorbances may be either molecular absorption, caused by molecular species in the light path, or merely physical scattering of the light by nonabsorbing species.

In the present work, nonatomic absorption was a general problem in the analyses of soil and peat samples. The matrices of these samples are quite complex and contain high concentrations of inorganic salts as well as organic matter which is only partially destroyed by the wet-ashing digestion procedure used. The use of a background correction system is essential in such analyses. The instruments used in this study were equipped with continuum-source background correction.

The basis of this method is a deuterium lamp, which produces an essentially continuous broad-band spectrum, especially between 200 and 300 nm . Using the assumption that the background absorption is continuous over the spectral bandwidth of the monochromator (0.2 - 1.0 nm), measurement of the total absorption is made with the analyte hollow cathode lamp, while measurement with the deuterium lamp gives the background absorption only. This is because the atomic absorption line is very narrow (≈0.002 nm) and hence makes virtually no contribution to the background absorption over the whole bandwidth. By electronically subtracting the deuterium lamp signal from the hollow cathode lamp signal, the analyte signal only may be obtained.

However, when the background is not a continuum but contains the fine structure of molecular electronic spectra, errors in background correction can occur. In this situation, the background absorption spectrum will consist of a number of narrow lines of varying intensity, overlapping the analyte resonance line to a greater or lesser extent. The continuum source method is rarely accurate in this case because the background absorption at the analyte wavelength will not necessarily match the average absorption

profile over the spectral bandpass measured with the deuterium lamp. Slavin and Carnrick (1986) document correction errors of this type.

Another common problem is that two separate optical systems are required, and these can easily become misaligned, thus viewing different parts of the sample vapour which is not necessarily homogeneous. Thus, the alignment of the lamps needs to be frequently checked. The technique of Zeeman background correction, which exploits Zeeman splitting of spectral lines in a magnetic field, is a preferable method if available.

Chemical interferences are the result of processes occurring in the flame which affect the ground state population of analyte atoms. One of the most common types is the formation of refractory (or thermally stable) compounds in the flame. An example encountered in the present work was the formation of calcium phosphate [$Ca_3(PO_4)_2$] in the air-acetylene flame, which depletes the ground state population of calcium atoms. This problem is usually easily overcome by using the hotter nitrous oxide-acetylene flame to dissociate the refractory compound, but this can lead to the second type of problem, which is thermal ionisation of ground state atoms. It is usually necessary to add an ionisation suppressant (an element with a lower ionisation potential than the analyte species). In the above example, calcium was found to be partially ionised in the hotter flame, so potassium was added as an ionisation suppressant.

It must be emphasised that flame AAS has many advantages that make it the method of choice when analyte solutions are sufficiently concentrated. Interferences are well-defined, and few problems were encountered in the analysis of lead, zinc, copper, manganese and cadmium in this study. The precision is very good (1-2%) and is limited by the reproducibility of flame conditions, which affect the population of ground state atoms. Another significant advantage is the speed of analysis. Determinations of individual solutions can be made in seconds, compared to minutes required for graphite furnace firings.

However, there are disadvantages of flame AAS which limit the usefulness of this technique. The nebuliser is only about 10% efficient; production of ground state atoms is not particularly efficient, and the lifetime of atoms in the light path is very short ($\approx 10^{-4}$ s). The overall effect of the above is that the number of atoms contributing to the analytical

signal is very small compared with the volume of solution used, and therefore the process is inefficient in terms of sample usage.

c) Graphite furnace AAS The advent of "flameless" atomisation greatly reduced these limitations. The principle of this technique was first suggested by L'vov (1959; in English translation in L'vov, 1984) and the first description of a furnace designed for analytical atomic absorption was by L'vov (1961). Massmann (1968) introduced a simpler furnace which is the basis for most current commercial instrumentation.

The basis of graphite furnace atomisation is that a small volume of solution (2 µl in this study) is injected into a small graphite tube clamped between electrodes, and rapidly heated by electrical resistance to vaporise the sample and produce a population of atoms. Particular advantages of this process are that volume wastage is virtually eliminated as the entire sample is vaporised, and the confined nature of the furnace leads to a dense population of atoms, thus increasing the analytical sensitivity markedly. This increase varies by 10^1 - 10^3 times over flame atomisation, depending on the element. However, precision is poorer (5-10%) and is limited by the reproducibility of sample introduction.

The inner surface of the graphite tube is coated with a thin (≈30 µm) layer of pyrolitic graphite. This is a dense, unreactive, anisotropic form of graphite and its presence has been found to greatly improve the performance of the furnace. Its functions are to stop the diffusion of hot gases out through the porous graphite; to discourage interactions of atoms with the carbon; and to prolong the lifetime of the furnace. With a pyrolitic layer, the determination of some refractory elements becomes possible, as their tendency to combine with the walls of the furnace, forming stable carbides, is significantly reduced.

Many interference effects have been described in the literature (e.g. Churella and Copeland, 1978; Czobik and Matousek, 1977, 1978; Smeyers-Verbecke et al., 1978; Slavin, 1988) and can be generally categorised as being physical or chemical in the mechanism by which they are produced.

Physical effects of viscosity and surface tension can affect the reproducibility of sample dispensing. The main effect is the degree to which the sample spreads inside the furnace. An improved design of furnace (Brodie, 1986) contains a partitioned central section to limit the spreading of the solvent and ensure that the sample dries reproducibly. Another physical effect is that of background absorption, which has been discussed in relation to flame atomisation. However, background absorption can often be separated from the analyte peak by a suitably-designed heating programme. This will be discussed shortly.

The types of chemical interferences encountered in flame atomisation are virtually absent from graphite furnace atomisation, but many other types have been described. The two main types are stable compound formation and volatile compound formation.

Stable compound formation is a problem for some refractory elements which have a tendency to form stable carbides with the walls of the furnace. This problem has been reduced by the use of pyrolitic graphite coatings; however, it is still not possible to successfully analyse tantalum, zirconium and tungsten for this reason.

Volatile compound formation is very common for metals such as zinc, lead and cadmium, and chloride ions are the major reported interfering species. Matousek and coworkers (Czobik and Matousek, 1977, 1978; Matousek and Brodie, 1973; Brodie and Matousek, 1974) have investigated this phenomenon and confirmed that the ground state analyte atom population is depleted by metal chloride formation in the vapour phase. Thus, these metals will volatilise and diffuse from the furnace before atomisation can take place. This problem was encountered in the present work, as it was found that cadmium in soil, peat and wood samples would begin to volatilise at around 300 °C.

This problem is usually overcome by the technique of matrix modification. Suitable matrix modifiers are added to convert the analyte to a form where it will atomise at a well-defined temperature well removed from the matrix absorption. In this study, the addition of H_3PO_4 was found to be very successful in removing chloride interference in the analysis of cadmium and lead in peat, wood and soil samples. Czobik and Matousek (1977) concluded that the addition of phosphoric acid produced refractory metal pyrophosphates which were found to atomise at higher temperatures, and with narrower

peak widths, than in the absence of phosphoric acid. The effect on the lead absorption profile of adding H_3PO_4 (0.01M) to a digested sample of hay powder is shown in Figure 7.1.

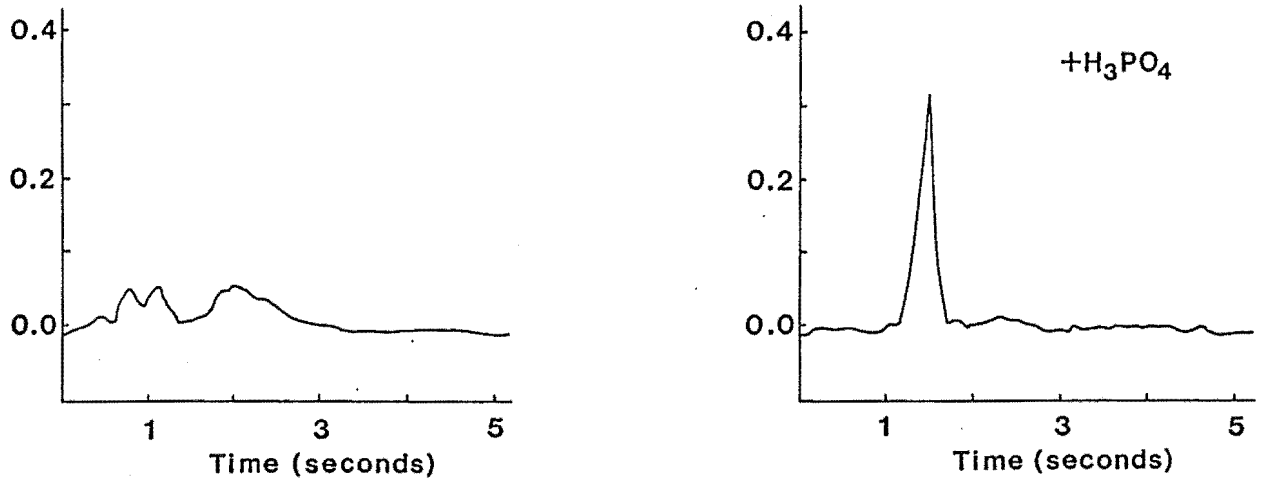

Figure 7.1 The effect of H_3PO_4 matrix modification on lead absorption signal of hay powder

The heating programme for the graphite furnace consists of three stages : drying, ashing, and atomisation of the sample. The overall aim in devising the heating programme is to maximise the analyte signal and remove it from matrix interferences.

During the drying stage, the solvent is volatilised, leaving the analyte and matrix deposited on the furnace wall. It was found to be necessary to evaporate the solvent slowly, without spattering, and a small mirror was used to observe that even drying was occurring. A slow ramp rate of 20 seconds up to 80°C, followed by ramping up to 120°C in 10 seconds, was found to produce even drying.

The second stage is the "ashing" process, during which most organic compounds decompose. As the furnace is maintained in an atmosphere of oxygen-free nitrogen to prevent oxidation of the graphite, the process occurring is actually pyrolysis rather than ashing. The choice of temperature is important, as it is a compromise between removing as much of the matrix as possible without losing any of the analyte. It was found that when H_3PO_4 was added as a modifier, complete ashing at around 400°C could be achieved with no loss of the analyte. The length of time required for ashing was dependent upon the nature of the sample matrix. Freeze-dried rainwater samples required

virtually no ashing, whereas the peat samples required 30 seconds ashing to remove the organic matrix.

The atomisation step requires rapid heating of the furnace to completely volatilise the analyte from its walls. Atomisation temperatures vary from element to element; the optimum temperature is considered to be the lowest one giving the maximum absorbance, as the lifetime of the furnace is prolonged at lower temperatures. Optimum temperatures were found to be 1600°C for cadmium; 1800°C for zinc and lead; 2200°C for copper, and 2300°C for manganese. The furnace must be maintained at the maximum temperature long enough to ensure complete volatilisation and diffusion of the samples, to prevent memory effects. A hold time of 1 second was found to be sufficient.

When the peak height is used for quantitation, sensitivity depends on the ramp rate up to the maximum temperature, because a fast heating rate produces a dense population of atoms (Koirtyohann and Kaiser, 1982). However, this varies with element volatility, as the less volatile elements such as copper show the greatest improvement in sensitivity with ramp rate. A maximum rate of 2000°C per second was attainable on the instrument used in this study, and this rate produced very sharp peaks. Hence, in general, peak heights rather than peak areas were used in this study because of the increased sensitivity.

d) Instrumentation Flame AAS analyses were perfomed on a Varian Techtron AA 1475 spectrophotometer, equipped with a continnum background correction system.

Graphite furnace AAS analyses were performed on a GBC 903 spectrophtometer, with a GBC 1000 controller, and a GF 1000 gas-flow regulator.

7.3.2 Anodic stripping voltammetry (ASV)

This technique was used in this study for the purpose of comparison with AAS measurements. A large sample of dustfall collected for study purposes was analysed by both ASV and AAS (with flame atomisation for lead, zinc, copper and manganese, and graphite furnace atomisation for cadmium). The results have been discussed in Section 2.3.

The equipment used in this study was a Princeton Applied Research PAR 174A Polarograph, with a Model 303 dropping mercury electrode and a Houston Omnigraphic 2000 X-Y chart recorder. Instrumental operating parameters are listed in Table 7.

Table 7. Operating parameters for the polarograph

Mode	:	D.C.
Deposition Potential	:	-1.3 V
Scan Direction	:	Positive
Scan Rate	:	20 mV/sec
Current Range	:	5 μA full scale for Pb, Zn, Cu 2 μA for Cd
Modulation Amplitude	:	25 mV
Output Offset	:	Off
Low Pass Filter	:	Off
Display Direction	:	Negative
Electrodeposition time	:	3 minutes
Rest Time	:	15 sec

ASV involves the electrodeposition of metals from a stirred solution into a microelectrode (in this case, a hanging mercury drop). After deoxygenating the cell by bubbling with oxygen-free nitrogen for ten minutes, a potential more negative than the reduction potential of the metals of interest is applied. Metal ions in solution are reduced and become amalgamated with the mercury, and a concentration of metals in the mercury drop, relative to the bulk solution, results. After a short electrodeposition period (typically between 2 and 10 minutes), a ramped linear potential in the positive direction is applied so that the electrodeposited metal is reoxidised and stripped out of the drop. A current results, the height of which is proportional to the concentration of metal in the bulk solution, and the position of which appears at a characteristic voltage for each metal.

One of the advantages of ASV is its multielement capacity and it was found that lead, zinc and copper could be be determined in a single scan, from -1.3 to +0.1 V, after plating at -1.3 V for 3 minutes. Although the reduction potential for cadmium occurs within this range, its much lower concentration meant that it was necessary to determine this metal separately, plating for 10 minutes and increasing the sensitivity. It is not possible to determine manganese in acid or neutral solutions because hydrogen evolution precedes the deposition of Mn^{2+} (Barendrecht, 1967).

The high acid strength of the digests presented a problem, because at low pH, the hydrogen overpotential is lowered on the mercury electrode, making the determination of zinc impossible. It was necessary to add a buffer (2 ml 1M acetate, pH 4.74) to restrict the pH to a suitable range. The presence of the buffer added to the reagent blank.

Although results obtained by ASV compared well to AAS measurements, it was decided to use the atomic absorption technique routinely throughout the this study due to the greater speed of analysis. Although the multielement capacity of ASV is an advantage, it does not detect manganese in acidic or neutral conditions, and the long periods required for deoxygenation and electroplating are time-consuming.

7.3.3 Instrumental neutron activation analysis (INAA)

INAA analyses were performed by Dr J.J. Fardy of CSIRO, Sydney, Australia. Between 100 and 200 mg of each sample were sealed in prewashed polyethylene vials, and placed in the inner site of a 15 MW DIDO reactor system. The samples were irradiatied for times of 1 minute and 9 hours, with thermal neutron fluxes of $5x10^{12}$ and $5x10^{13}$ $n.cm^2.s^{-1}$ respectively. The samples irradiated for 1 minute were allowed 20 minutes decay, then were counted for 10 minutes with a Ge(Li) γ-ray detector with an efficiency of 15% and a resolution of 2.1 keV for the 1332 keV peak of ^{60}Co. The nuclides detected by this procedure were ^{27}Mg, ^{28}Al, ^{38}Cl, ^{49}Ca, ^{51}Ti, ^{52}V, ^{56}Mn, ^{80}Br, ^{87}Sr, ^{128}I, ^{139}Ba, ^{165}Dy, ^{24}Na, ^{42}K, ^{72}Ga, and ^{152}Eu.

Samples irradiated for 9 hours were allowed 3-4 days cooling then were counted for 2 hours with a Ge(Li) γ-ray detector with an efficiency of 20% and a resolution of 1.8 keV for the 1332 keV peak. This procedure was used to measure ^{76}As, ^{82}Br, ^{122}Sb, ^{140}La, ^{153}Sm, ^{175}Yb, ^{177}Lu, ^{187}W, ^{198}Au, ^{239}Nb, ^{46}Sc, ^{51}Cr, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{86}Rb, ^{85}Sr, ^{95}Zr, ^{131}Ba, ^{134}Cs, ^{141}Ce, ^{147}Nd, ^{152}Eu, ^{160}Tb, ^{169}Yb, ^{181}Hf, ^{182}Ta and ^{233}Po.

The gamma-ray spectra were stored and processed on an IBM 370 computer. N.B.S. reference standards SRM 1632 (coal) and 1633 (fly-ash) were used as calibrants.

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Appendix

Chapter 3

Conversion table between units of deposition

Unit*	ng/cm^2/day	µg/cm^2/yr	µg/m^2/day	mg/m^2/yr	kg/ha/yr
ng/cm^2/day	1	-	-	-	-
µg/cm^2/yr	2.73	1	-	-	-
µg/m^2/day	0.1	0.0365	1	-	-
mg/m^2/yr	0.273	0.1	2.73	1	-
kg/ha/yr	27.3	10	273	100	1

* Conversion figures are applied to data in units in the lefthand column to convert to the appropriate units in the top row.

3.1 Deposition data

Each data point is the deposition flux versus the appoximate midpoint of the sampling interval.

Lead (µg/m^2/day)

Date	W1	W2	W3	W4	W5	W6	W7	S1	S2	S3	S4	N1	N2	N3	N4	P1	C1	C2	C3
Dec 85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jan 86	-	77	71	59	-	-	-	88	94	70	81	48	20	93	73	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Apr	57	63	51	33	-	-	-	129	63	81	82	43	-	-	45	-	-	-	-
May	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	31	456	110	213
Jun	-	-	-	-	30	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jul	119	114	109	84	-	98	-	170	-	107	95	-	-	-	-	-	514	227	183
Aug	-	-	-	-	-	-	-	-	-	-	-	42	58	-	77	30	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	401	308	172
Oct	89	60	67	57	-	-	-	93	-	87	79	-	-	-	-	-	-	-	-
Nov	-	-	-	-	-	-	-	-	-	-	-	30	50	-	50	39	-	-	-
Dec	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	290	84	80
Jan 87	59	44	43	37	-	-	-	48	-	78	36	-	-	-	-	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	19	76	-	-	-	-	-	25	51	-	32	29	188	95	119
Apr	78	49	52	51	-	-	-	76	-	59	61	-	-	-	-	-	-	-	-
May	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	210	134	160
Jun	-	-	-	-	-	-	-	-	-	-	-	25	-	-	14	26	-	-	-
Jul	84	81	84	68	-	-	1.9	89	95	72	-	-	-	-	-	-	-	-	-
Aug	-	-	-	-	-	20	-	-	-	-	-	-	-	-	-	-	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	43	-	35	34	-	-	-	-
Oct	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nov	77	65	67	57	-	-	-	61	-	54	54	-	-	-	-	-	-	-	-
Dec	-	-	-	-	14	-	1.9	-	-	-	-	47	-	33	40	-	-	-	-
Jan 88	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Feb	61	42	50	54	-	-	-	59	-	50	60	-	-	-	-	-	-	-	-
Mar	-	-	-	-	-	-	-	-	-	-	-	58	-	37	21	-	-	-	-
Apr	-	-	-	-	18	-	1.6	-	-	-	-	-	-	-	-	-	-	-	-

Zinc ($\mu g/m^2/day$)

Date	W1	W2	W3	W4	W5	W6	W7	S1	S2	S3	S4	N1	N2	N3	N4	P1	C1	C2	C3
Dec 85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jan 86	-	12	18	14	-	-	-	21	11	12	16	18	25	22	16	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Apr	22	19	16	14	-	-	-	-	44	38	9.5	14	-	-	13	-	-	-	-
May	-	-	-	-	-	-	-	48	-	-	-	-	-	-	-	-	255	94	196
Jun	-	-	-	-	4.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jul	33	32	29	35	-	5.0	-	-	-	39.1	19	-	-	-	-	-	355	137	131
Aug	-	-	-	-	-	-	-	-	-	-	-	7.4	22	-	14	12	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	201	131	29
Oct	19	22	16	15	-	-	-	25	-	25	14	-	-	-	-	-	-	-	-
Nov	-	-	-	-	-	-	-	-	-	-	-	17	21	-	27	11	-	-	-
Dec	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	160	120	75
Jan 87	18	14	20	14	-	-	-	14	-	15	6.9	-	-	-	-	-	-	-	-
Feb	-	-	-	-	-	10	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	4.9	-	-	-	-	-	-	5.2	24	-	6.0	8.4	147	80	59
Apr	7.5	12	16	2.5	-	-	-	17	-	10	10	-	-	-	-	-	-	-	-
May	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	246	36	89
Jun	-	-	-	-	-	-	-	-	-	-	-	11	-	-	3.8	12	-	-	-
Jul	21	32	24	21	-	-	-	30	-	23	24	-	-	-	-	-	-	-	-
Aug	-	-	-	-	12	-	1.2	-	-	-	-	-	-	-	-	-	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	15	-	-	14	14	-	-	-
Oct	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nov	19	37	44	14	-	-	-	23	-	14	14	-	-	-	-	-	-	-	-
Dec	-	-	-	-	10	-	3.9	-	-	-	-	9.5	-	-	6.8	20	-	-	-
Jan 88	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Feb	10	12	9.9	11	-	-	-	16	-	11	14	-	-	-	-	-	-	-	-
Mar	-	-	-	-	-	-	-	-	-	-	-	6.9	-	-	9.6	37	-	-	-
Apr	-	-	-	-	11	-	1.5	-	-	-	-	-	-	-	-	-	-	-	-

Copper ($\mu g/m^2/day$)

Date	W1	W2	W3	W4	W5	W6	W7	S1	S2	S3	S4	N1	N2	N3	N4	P1	C1	C2	C3
Dec 85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jan 86	-	2.7	1.7	1.5	-	-	-	-	5.4	4.5	.86	1.7	1.4	1.0	4.1	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Apr	5.5	6.3	5.4	2.3	-	-	-	12	5.3	5.4	4.6	2.4	2.0	-	2.9	-	-	-	-
May	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	22	5.9	7.8
Jun	-	-	-	-	2.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jul	7.1	6.7	3.9	4.6	-	2.0	-	2.4	-	7.2	7.7	-	-	-	-	-	25	11	10
Aug	-	-	-	-	-	-	-	-	-	-	-	6.5	5.9	-	5.6	2.4	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	22	12	8.9
Oct	5.7	3.9	3.0	2.0	-	-	-	5.2	-	3.1	5.8	-	-	-	-	-	-	-	-
Nov	-	-	-	-	-	-	-	-	-	-	-	6.0	4.5	-	4.0	10	-	-	-
Dec	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9.0	6.0	8.6
Jan 87	3.6	1.7	1.3	1.9	-	-	-	5.4		-1.5	2.6	-	-	-	-	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	4.4	3.5	-	-	-	-	-	4.8	5.2	-	1.9	5.9	23	17	13
Apr	4.1	3.2	3.4	0.61	-	-	-	2.8	-	1.5	4.5	-	-	-	-	-	-	-	-
May	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	25	11	7.2
Jun	-	-	-	-	-	-	-	-	-	-	-	2.8	-	-	2.4	2.0	-	-	-
Jul	8.2	6.1	5.9	4.6	-	-	0.93	4.9	-	7.9	7.2	-	-	-	-	-	-	-	-
Aug	-	-	-	-	4.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	1.5	-	-	1.0	2.2	-	-	-
Oct	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nov	5.3	4.5	4.4	2.0	-	-	-	6.6	-	3.7	3.1	-	-	-	-	-	-	-	-

Copper ($\mu g/m^2/day$) - continued

Date	W1	W2	W3	W4	W5	W6	W7	S1	S2	S3	S4	N1	N2	N3	N4	P1	C1	C2	C3
Dec	-	-	-	-	5.0	-	1.2	-	-	-	-	2.7	-	-	1.5	3.7	-	-	-
Jan 88	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Feb	4.0	1.6	4.0	2.6	-	-	-	13	-	4.1	4.8	-	-	-	-	-	-	-	-
Mar	-	-	-	-	-	-	-	-	-	-	-	9.2	-	-	2.1	3.6	-	-	-
Apr	-	-	-	-	1.0	-	0.35	-	-	-	-	-	-	-	-	-	-	-	-

Manganese ($\mu g/m^2/day$)

Date	W1	W2	W3	W4	W5	W6	W7	S1	S2	S3	S4	N1	N2	N3	N4	P1	C1	C2	C3
Dec 85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jan 86	-	23	25	20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Apr	25	24	32	20	-	-	-	-	38	18	18	13	-	-	23	-	-	-	-
May	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	25	11	17
Jun	-	-	-	-	46	-	-	54	36	-	-	-	-	-	-	-	-	-	-
Jul	33	11	43	31	-	13	-	-	-	33	24	-	-	-	-	-	21	4.6	-
Aug	-	-	-	-	-	-	-	-	-	-	-	20	15	-	26	20	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	16	30	-
Oct	29	31	15	8.3	-	-	-	23	-	11	11	-	-	-	-	-	-	-	-
Nov	-	-	-	-	-	-	-	-	-	-	-	14	20	-	24	14	-	-	-
Dec	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	26	40	-
Jan 87	25	26	19	12	-	-	-	27	-	6.8	17	-	-	-	-	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	13	12	-	-	-	-	-	10	15	-	26	20	28	26	-
Apr	9.9	17	10	34	-	-	-	29	-	15	17	-	-	-	-	-	-	-	-
May	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	19	20	-
Jun	-	-	-	-	-	-	-	-	-	-	-	28	-	-	12	26	-	-	-
Jul	23	29	23	33	-	-	11	13	-	24	28	-	-	-	-	-	-	-	-
Aug	-	-	-	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	38	-	-	16	23	-	-	-
Oct	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nov	24	19	22	6.9	-	-	-	25	-	12	27	-	-	-	-	-	-	-	-
Dec	-	-	-	-	19	-	34	-	-	-	-	19	-	-	19	15	-	-	-
Jan 88	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Feb	21	-	-	20	-	-	-	44	-	15	15	-	-	-	-	-	-	-	-
Mar	-	26	34	-	-	-	-	-	-	-	-	-	-	21	-	-	21	27	-
Apr	-	-	-	-	52	-	17	-	-	-	-	-	-	-	-	-	-	-	-

Cadmium ($\mu g/m^2/day$)

Date	W1	W2	W3	W4	W5	W6	W7	S1	S2	S3	S4	N1	N2	N3	N4	P1	C1	C2	C3
Dec 85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jan 86	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Apr	.19	.29	.28	.40	-	-	-	.50	.51	.12	.29	.19	.16	-	.31	-	-	-	-
May	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.16	4.3	5.1	3.1
Jun	-	-	-	-	.020	-	-	.88	-	-	-	-	-	-	-	-	-	-	-
Jul	.62	.49	.70	.61	-	.022	-	-	.79	.91	.90	-	-	-	-	-	9.8	6.1	5.0
Aug	-	-	-	-	-	-	-	-	-	-	-	.46	.24	-	.35	.11	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.1	2.2	-
Oct	.45	.71	.60	.30	-	-	-	.60	.40	.40	.31	-	-	-	-	-	-	-	-
Nov	-	-	-	-	-	-	-	-	-	-	-	.23	.20	-	.15	.27	-	-	-

Cadmium (µg/m^2/day) - continued

Date	W1	W2	W3	W4	W5	W6	W7	S1	S2	S3	S4	N1	N2	N3	N4	P1	C1	C2	C3
Dec	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.7	3.3	2.5
Jan 87	.47	.49	.19	.32	-	-	-	.38	.21	.19	.18	-	-	-	-	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	-	-	-	-	.014	.026	-	-	-	-	-	.44	.38	-	.27	.27	1.0	2.2	2.4
Apr	.44	.20	.62	.21	-	-	-	.30	-	.27	.23	-	-	-	-	-	-	-	-
May	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8.6	6.7	3.8
Jun	-	-	-	-	-	-	-	-	-	-	-	.19	-	-	.41	.17	-	-	-
Jul	.51	.66	.61	.46	-	-	.0059	.96	-	.74	.58	-	-	-	-	-	-	-	-
Aug	-	-	-	-	.025	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sep	-	-	-	-	-	-	-	-	-	-	-	.25	-	-	.22	.22	-	-	-
Oct	-	-	-	-	-	-	-	.48	-	-	-	-	-	-	-	-	-	-	-
Nov	.50	.51	.25	.12	-	-	-	-	-	.41	.54	-	-	-	-	-	-	-	-
Dec	-	-	-	-	.0050	-	.0069	-	-	-	-	.35	-	-	.39	.50	-	-	-
Jan 88	-	-	-	-	-	-	-	.44	-	-	-	-	-	-	-	-	-	-	-
Feb	.33	.29	.19	.51	-	-	-	-	-	.30	.33	-	-	-	-	-	-	-	-
Mar	-	-	-	-	-	-	-	-	-	-	-	.59	-	-	.37	.22	-	-	-
Apr	-	-	-	-	.0091	-	.0045	-	-	-	-	-	-	-	-	-	-	-	-

3.2 Soluble/insoluble deposition data

The units of the deposition data are µg/container.

Site + Date	Rainfall* (mm)	pH	Pb			Zn			Cu		
			sol	insol	%soluble	sol	insol	%soluble	sol	insol	%soluble
W1 Jun-Sep	162	3.6	68	155	30	26	39	40	2.1	7.6	22
W2 Jun-Sep	162	3.8	73	160	30	46	78	37	0.66	3	12
W3 Jun-Sep	162	4.7	30	156	16	13	45	23	0.21	1.7	11
W4 Jun-Sep	162	5.5	x	144	x	x	39	x	x	1.1	x
W2 Oct-Dec	118	7.3	0.71	114	0.6	18	57	24	0.77	6.9	10
W3 Oct-Dec	118	6.1	3.6	102	3.4	15	67	18	0.63	6.7	6
W4 Oct-Dec	118	6.3	7.2	86	7.7	6	22	21	0.48	3.1	11
W1 Jan-Mar	115	6.8	2.7	142	1.9	5	20	21	1.3	16.5	7.3
W2 Jan-Mar	62	5.4	3.4	54	11.2	1.1	3.1	27	1.6	7.8	11
W3 Jan-Mar	62	5.8	8.1	64	5.9	4.6	13	26	1.8	14.1	11
W4 Jan-Mar	115	6.6	7.8	109	6.7	5.5	23	24	1.8	13.3	12
W5 Apr-Sep	150	7.1	0.49	37	1.3	6.9	23.6	22.6	1.2	19	5.9
W7 Apr-Sep	246	7.1	0.47	4.7	9.1	0.12	1.2	9.1	0.23	2.3	9.1
W5 Oct-Mar	256	7.1	1.6	41	3.7	5	31	14	0.48	14.8	3.1
W7 Oct-Mar	470	6.4	0.11	5.8	1.9	0.34	12	2.8	0.38	3.6	9.5
W5 Apr-Jun	154	7.2	2.1	35.6	5.6	1.6	22.2	6.6	1.5	17.9	7.7
W7 Apr-Jun	214	6.3	0.37	3.23	10.2	2.9	0.4	12	0.077	0.7	10
S1 Jun-Aug	162	6.1	5.1	202	2.5	11.5	51	20	1.2	4.8	15
S3 Jun-Aug	162	6.4	10.3	161	6	5.8	39	13	1.6	13.4	11
S4 Jun-Aug	162	7.3	9.6	123	7.2	4.5	24	15.9	1.1	7.6	13
S1 Sep-Dec	136	6.9	0.96	106	0.9	12	40	23	0.99	4.9	17
S3 Sep-Dec	136	6.0	11.1	95	10.5	11	24	31	0.7	3.7	16
S4 Sep-Dec	136	6.1	1.4	94	1.5	5	25	16	0.4	3.1	11
S1 Jan-Mar	62	4.0	44.9	113	28.4	13	20	39	4.2	16.9	20
S3 Jan-Mar	62	5.7	25.	101	10.4	7	23	23	1.1	8.2	12
S4 Jan-Mar	115	6.0	8.3	121	6.4	12	48.4	20	1.1	9.6	10
N1 Aug-Oct	98	6.2	3.1	75	4	6.1	26	19	0.32	2.6	11
N4 Aug-Oct	98	6.0	1.9	61	3	5.3	24	18	0.29	1.8	14
P1 Aug-Oct	98	5.2	9.8	58	14.4	6.6	23.3	22	0.22	2	10
N1 Nov-Jan	89	6.9	8.8	82	9.7	5.3	17	24	1	4.7	18

Site + Date	Rainfall* (mm)	pH	Pb			Zn			Cu		
			sol	insol	%soluble	sol	insol	%soluble	sol	insol	%soluble
N4 Nov-Jan	89	6.4	2.9	58	4.8	5.3	12	29	0.24	2.6	8.5
P1 Nov-Jan	89	6.1	4	70	5.4	7	34	17	0.67	6.4	9.5
N1 Feb-Apr	71	6.6	5.9	79	6.9	1.3	9.4	12.1	1.4	12.5	10
N4 Feb-Apr	71	6.7	0.43	50	0.9	4	13.1	23.4	0.4	2.8	12
P1 Feb-Apr	71	6.0	2.1	29	6.8	18	50.4	26	1.4	12.5	10

Site /Date	Mn			Cd		
	sol	insol	%soluble	sol	insol	%soluble
W1 Jun-Sep	10.8	43	20	0.14	0.95	13
W2 Jun-Sep	3.7	54	6.4	0.095	1.23	7.2
W3 Jun-Sep	4.2	43	9.3	0.026	1.13	2.2
W4 Jun-Sep	x	60	x	x	1.6	x
W2 Oct-Dec	5.7	30	16	0.087	0.78	10.8
W3 Oct-Dec	6.5	33	16	0.048	0.39	10.9
W4 Oct-Dec	1.8	11	14	0.014	0.18	7
W1 Jan-Mar	5	43	10	0.056	0.67	7.7
W2 Jan-Mar	4	34	7.9	0.008	0.37	2.1
W3 Jan-Mar	6	44	12	0.025	0.24	9.4
W4 Jan-Mar	6	40	13	0.036	1.03	3.4
W5 Apr-Sep	2.5	27	8.5	0.0027	0.046	5.6
W7 Apr-Sep	0.017	21	0.8	0.0059	0.015	3.8
W5 Oct-Mar	2.9	55	5	0.00072	0.016	4.3
W7 Oct-Mar	1	104	0.9	0.0017	0.021	7.4
W5 Apr-Jun	7.6	102	6.9	0.0014	0.018	7.1
W7 Apr-Jun	0.09	34	0.2	0.0002	0.009	2.2
S1 Jun-Aug	5	22	19	0.236	1.63	12.6
S3 Jun-Aug	0.96	40	2.2	0.024	1.26	1.9
S4 Jun-Aug	0.18	47	0.3	0.044	0.99	4.2
S1 Sep-Dec	1.2	43	2.7	0.012	0.84	1.4
S3 Sep-Dec	1.8	21	8.2	0.029	0.72	3.9
S4 Sep-Dec	1.7	48	3.4	0.026	0.95	3.9
S1 Jan-Mar	0.3	56	0.5	0.1	0.56	15
S3 Jan-Mar	3	30	9.1	0.04	0.61	6.2
S4 Jan-Mar	4	31	11	0.016	0.67	2.3
N1 Aug-Oct	1.2	67	1.7	0.019	0.43	4.2
N4 Aug-Oct	0.9	27	3.2	0.029	0.38	7.1
P1 Aug-Oct	2.7	40	6.3	0.025	0.37	6.3
N1 Nov-Jan	2.8	33	7.8	0.046	0.61	7
N4 Nov-Jan	1.5	33	4.3	0.009	0.68	1.3
P1 Nov-Jan	4	26	13.3	0.051	0.88	5.5
N1 Feb-Apr	0.7	29	2.4	0.0031	0.8	0.3
N4 Feb-Apr	0.3	24	1.2	0.0061	0.5	1.2
P1 Feb-Apr	1.5	37	3.9	0.055	3	15.5

x Data not available because flask shattered on freeze-drier

* Rainfall is the approximate total input to the site during the sampling period, estimated from Meteorological Office data.

Chapter 5

5.1 Wanganui River Flats Tree 1.

Year*	Dry-weight concentration(μg/g) of ring wood					
	Ring mass(g)	Pb	Zn	Cu	Mn	Cd
1984	.0979	.16	2.9	2.0	43.4	.070
1975	.0850	.15	2.9	1.5	51.0	.061
1965	.0544	.19	1.5	1.8	52.6	.048
1955	.0519	.18	2.2	1.4	55.2	.046
1940	.0820	.10	2.2	1.2	61.9	.095
1915	.1050	.049	2.9	1.8	68.8	.034
1895	.0485	.15	2.4	1.3	73.4	.017
1885	.0678	.051	2.8	1.8	61.5	.017
1875	.0674	.045	3.1	1.5	65.9	.023
1865	.0650	.047	3.4	1.5	60.9	.048
1855	.0579	.060	5.0	1.7	71.3	.039
1845	.0574	.11	5.0	1.3	64.2	.059
1835	.0664	.068	2.4	1.0	59.3	.018
1825	.0831	.19	2.9	2.1	69.7	.017
1815	.0633	.070	2.0	1.9	62.9	.015
1805	.0540	.12	2.5	2.4	58.8	.016
1795	.0389	.17	4.3	4.1	86.6	.024
1775	.0678	.14	2.5	.59	61.5	.054
1765	.0907	.078	2.4	1.6	60.3	.038
1755	.0593	.14	2.8	1.6	60.0	.087
1745	.0813	.12	3.7	2.0	62.1	.085
1735	.1166	.15	4.0	.89	56.0	.037
1725	.0804	.16	3.0	1.5	57.6	.020
1715	.0898	.078	4.6	1.4	49.0	.029
1705	.0946	.13	6.4	1.3	49.6	.064
1695	.1593	.19	1.2	2.2	38.3	.054
1685	.1494	.16	2.4	2.2	72.1	.023
1675	.1635	.11	2.8	1.1	66.7	.021
1665	.3053	.045	5.4	1.2	37.7	.042
1655	.3168	.052	6.5	1.2	41.7	.027

* Year given is midpoint of interval

5.2 Wanganui River Flats Tree 2.

Year	Dry-weight concentration(μg/g)					
	Ring mass(g)	Pb	Cu	Zn	Mn	Cd
1984	.0967	.039	2.9	1.8	37	.074
1975	.0573	.033	2.3	1.7	34.2	.042
1965	.0681	.056	4.9	2.0	42.5	.025
1950	.0377	.030	6.2	1.4	75.2	.064
1930	.0800	.12	3.6	1.6	77.6	.050
1915	.0548	.01	6.8	1.4	71.4	.088
1905	.0400	.076	1.7	1.4	80.9	.066
1890	.0819	.084	2.5	1.4	71.8	.021
1875	.0426	.12	3.7	3.3	87.9	.035
1865	.0473	.11	2.7	2.0	82.8	.051
1855	.0761	.050	3.9	1.4	78.3	.077
1845	.0909	.11	2.8	1.4	66.5	.053
1835	.0954	.086	2.5	1.5	64.2	.059
1825	.1200	.059	1.2	1.6	49.7	.033
1815	.1359	.017	2.6	1.5	57.1	.032
1805	.0787	.18	3.1	2.0	78.8	.055
1795	.1023	.069	1.3	1.2	50.3	.044
1785	.0489	.15	2.5	4.4	100.2	.049

5.2 Wanganui River Flats tree 2 - continued

Year	Ring mass(g)	Dry-weight concentration(µg/g) Pb	Cu	Zn	Mn	Cd
1775	.0729	.058	2.6	1.8	68.3	.033
1765	.0770	.055	4.9	1.4	65.7	.031
1755	.0921	.15	2.9	2.0	93.1	.061
1745	.1569	.074	1	2.8	74.9	.092
1735	.1315	.058	1.1	2.8	44.1	.055

5.3 Wanganui River Flats Tree 3.

Year	Ring mass(g)	Dry-weight concentration(µg/g) Pb	Zn	Cu	Mn	Cd
1984	.0879	.29	5.0	4.9	56.8	.092
1975	.0464	.041	4.4	1.9	35.4	.058
1960	.0455	.031	3.7	1.6	52.6	.081
1940	.0305	.15	3.0	2.1	111	.100
1920	.0525	.12	4.5	1.7	67.2	.026
1905	.0617	.16	2.0	1.3	52.1	.020
1895	.0377	.13	3.0	1.1	62.8	.063
1885	.0457	.053	3.7	1.7	65.0	.041
1870	.0525	.037	.77	2.1	60.7	.046
1855	.0353	.043	.64	3.5	69.1	.084
1845	.034	.18	1.3	3.1	68.2	.047
1835	.0576	.11	.99	2.1	69.6	.110
1825	.0395	.19	.86	2.8	61.8	.043
1810	.0668	.13	2.2	2.3	68.2	.063
1795	.0368	.17	2.8	2.1	53.6	.090
1785	.0826	.10	1.1	5.1	90.7	.073
1775	.0394	.19	2.3	4.9	55.9	.022
1765	.1004	.10	2.8	3.2	87.6	.029
1755	.0715	.13	.65	2.8	84.1	.032
1745	.0572	.05	4.8	2.6	98.4	.036
1735	.0669	.13	3.7	2.4	71.5	.070
1725	.0724	.20	3.0	5.9	64.7	.057
1715	.1046	.15	3.0	1.8	83.1	.091
1705	.0978	.19	3.4	1.2	79.8	.075
1695	.1136	.16	3.6	1.6	57.0	.093
1685	.1086	.12	3.2	2.0	82.3	.048
1675	.171	.11	3.3	3.9	103	.086
1665	.1207	.21	3.2	3.6	55.4	.070
1655	.1547	.26	3.5	3.4	69.9	.050

5.4 Riccarton Bush Tree 1 - NW core

Year	Ring mass(g)	Dry-weight concentration(µg/g) Cu	Zn	Mn	Pb	Cd
1979	.1289	10.6	13.8	22	3.3	.22
1965	.1454	8.9	8.5	21	2.8	.14
1955	.1011	7.2	6.1	25	2.7	.16
1945	.0659	7.9	8.8	15	2.4	.11
1935	.1054	6.3	3.8	21	2.8	.10
1925	.1072	4.9	2.8	17	1.4	.096
1915	.1149	5.2	2.2	13	.75	.11

5.4 Riccarton Bush Tree 1 - NW core - continued

Year	Dry-weight concentration(µg/g)					
	Ring mass(g)	Cu	Zn	Mn	Pb	Cd
1905	.1654	5.3	4.0	20	.76	.15
1895	.1896	3.3	2.8	21	.49	.12
1885	.2297	3.3	2.6	22	.59	.090
1875	.1368	4.5	4.3	23	.41	.052
1865	.1495	3.6	4.0	24	.51	.034
1855	.1826	4.1	3.0	25	1.1	.020
1845	.1629	3.0	3.5	29	.35	.022
1835	.1413	2.6	2.6	37	.25	.032
1825	.1794	2.8	3.6	41	.25	.030
1810	.1778	2.9	3.4	33	.29	.029
1790	.1879	2.4	2.8	44	.33	.030
1770	.1795	1.9	1.6	41	.37	.027
1750	.2314	1.6	1.3	20	.26	.025
1730	.1877	1.4	1.2	35	.19	.025

5.5 Riccarton Bush Tree 1 - SE core

Year	Dry-weight concentration(µg/g)					
	Ring mass(g)	Cu	Zn	Mn	Pb	Cd
1973	.2605	10.6	10.1	20	3.2	.19
1950	.1318	7.7	7.7	20	2.7	.17
1930	.1353	5.5	3.6	15	2.0	.096
1915	.1224	5.3	2.2	14	.73	.11
1905	.1165	5.3	4.1	19	.77	.18
1895	.1916	3.1	2.6	22	.47	.14
1885	.2059	3.6	2.8	21	.58	.078
1875	.2158	4.4	4.5	21	.42	.034
1865	.1770	3.6	4.0	23	.51	.034
1855	.1258	4.3	3.8	25	1.1	.032
1845	.1494	3.1	3.6	29	.29	.027
1835	.1063	2.7	2.5	38	.26	.038
1825	.0968	2.9	3.6	42	.22	.031
1810	.1711	3.0	3.3	33	.08	.035
1790	.1382	2.5	2.7	45	.65	.036
1770	.0957	1.8	1.5	42	.21	.022
1750	.1592	1.6	1.3	20	.25	.028
1730	.0962	1.5	1.5	34	.31	.029
1710	.0955	3.1	2.9	55	.16	.021
1690	.1218	2.6	2.3	44	.57	.031
1670	.1256	5.8	2.2	33	.43	.033

5.6 Riccarton Bush Tree 2 - N core

Year	Ring mass(g)	Dry-weight concentration(µg/g) Cu	Zn	Mn	Pb	Cd
1984	.1683	12.0	13.2	20	4.6	.23
1975	.1367	9.9	11.1	21	4.3	.21
1955	.1680	8.0	9.6	23	2.3	.17
1945	.2104	7.5	7.9	18	2.9	.14
1915	.1338	4.5	4.2	15	.76	.12
1905	.1305	4.9	4.0	19	.85	.17
1885	.0681	3.6	3.0	22	.57	.062
1850	.1485	4.5	4.2	28	.94	.042
1815	.1026	3.2	3.1	30	.55	.044
1805	.1237	2.7	2.9	35	.46	.029
1795	.1000	2.6	2.6	45	.58	.031
1765	.1078	1.6	1.4	42	.33	.025

5.7 Riccarton Bush Tree 2 - S core

Year	Ring mass(g)	Dry-weight concentration(µg/g) Cu	Zn	Mn	Pb	Cd
1975	.1725	10	11.3	21	4.3	.210
1925	.2013	4.4	5.1	16	1.2	.093
1820	.1636	2.7	3.6	38	.14	.035
1740	.1367	1.5	1.6	26	.22	.022
1705	.1111	1.6	2.0	51	.19	.030
1695	.0923	2.0	1.9	46	.21	.020

5.8 Riccarton Bush Tree 3 - NW core

Year	Ring mass(g)	Dry-weight concentration(µg/g) Cu	Zn	Mn	Pb	Cd
1983	.1607	10.7	14.4	17	4.0	.24
1973	.2018	8.9	13.9	19	3.8	.20
1963	.1398	8.6	10.1	20	2.9	.20
1953	.0977	5.2	9.8	21	2.4	.18
1943	.1062	6.0	6.9	20	2.6	.15
1933	.1031	3.7	3.6	16	2.5	.10
1923	.1607	3.8	3.8	15	1.6	.09
1913	.1819	3.1	2.5	14	.82	.12
1903	.1901	4.9	4.0	19	.72	.15
1893	.1763	3.1	2.8	23	.47	.13
1883	.1112	4.4	2.7	20	.57	.07
1873	.1346	4.4	4.3	21	.41	.05
1858	.2701	4.2	3.8	25	1.2	.03
1843	.1329	3.1	3.5	29	.31	.06
1833	.1366	2.5	2.6	36	.28	.04
1823	.1957	2.4	3.5	40	.21	.03
1813	.1366	2.6	3.7	34	.15	.04
1803	.1561	2.9	3.5	38	.11	.03
1788	.1603	2.8	2.2	47	.19	.03
1768	.2235	2.0	1.6	43	.22	.05
1748	.1834	1.7	1.2	23	.14	.06

5.9 INAA data - Wanganui River Flats Tree 2

Year	Ring mass(g)	Dry-weight concentration(μg/g) Zn	Mn
1984	.0703	3.0	57.2
1975	.0700	2.57	69.7
1965	.0635	1.96	79.1
1955	.0721	1.85	89.0
1945	.0859	1.80	97.6
1935	.0500	2.27	117
1925	.0516	1.17	98.6
1910	.0644	1.8	118
1890	.0639	1.68	140
1875	.1091	-	-
1865	.0544	3.0	136
1855	.0673	3.4	124
1845	.0504	5.7	123
1835	.0538	5.7	114
1825	.0424	5.2	115
1815	.0824	2.3	110
1805	.0856	2.2	120
1795	.1233	3.2	102
1780	.0871	4.4	109
1765	.0656	4.2	122
1755	.0446	3.0	124
1745	.0467	4.0	139
1735	.0613	2.41	127
1725	.0740	1.91	113
1715	.0854	1.67	111
1700	.0890	-	106
1685	.0848	2.7	88.4

5.10 Riccarton Bush Soil Core (18.7.88)

a) Core descriptions

Classification: Tai Tapu Silt Loam

Core 1				Core 2			
Depth	Horizon	Texture*	Colour	Depth	Horizon	Texture	Colour
0-8cm	Ah_1	Silt Loam	Dark brown	0-9cm	Ah_1	Silt Loam	Dark brown
8-22	Ah_2	Clay Loam	Paler brown	9-18	Ah_2	Clay Loam	Paler brown
22-63	C_r	Clay Loam	Fawn/grey	18-58	C_r	Clay Loam	Fawn/grey
63-75	$2C_r$	Sandy Clay Loam	Reddish grey	58-72	$2C_r$	Silty Clay Loam	Red/grey
75-85	$3C_r$	Loamy Sand	Dark grey	72-84	$3C_r$	Sandy Clay Loam	Red/grey
				84+	$4C_r$	Loamy Sand	Dark grey

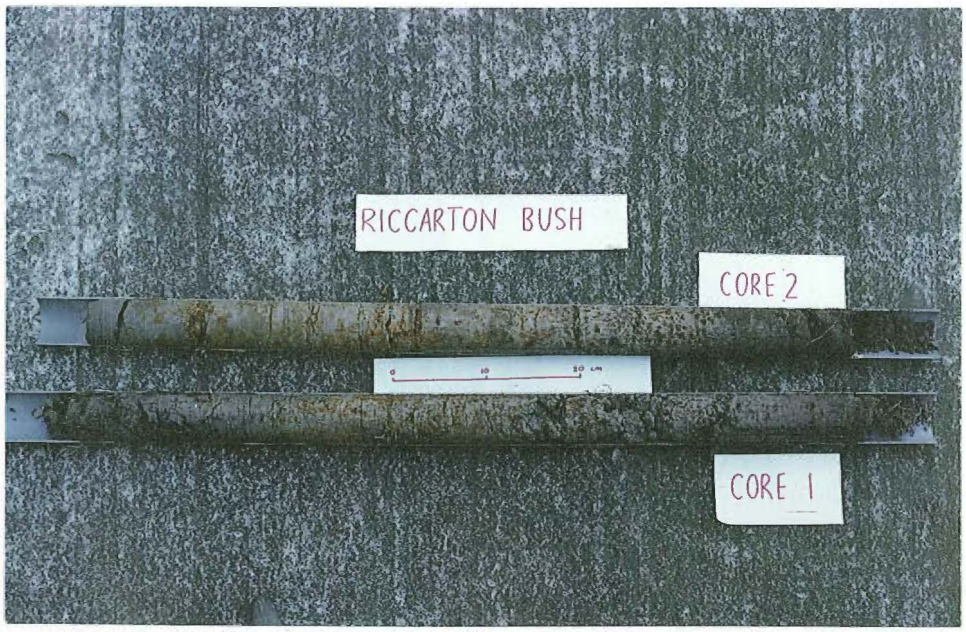
*based on field methods

b) Colour classification based on Munsell Book of Colour

Depth (cm)	Core 1 Major	Minor	Core 2 Major	Minor
0-5	10YR 3/2		2.5Y 3/2	
5-10	10YR 4/2		2.5Y 3/2	
10-15	2.5Y 5/2		2.5Y 4/2	
15-20	2.5Y 5/2		2.5Y 5/2	
20-25	2.5Y 5/2		2.5Y 5/4	2.5Y 3/2
25-30	2.5Y 5/2		2.5Y 5/4	2.5Y 3/2
30-35	2.5Y 5/2		2.5Y 6/4	
35-40	2.5Y 5/2		2.5Y 6/4	
40-45	2.5Y 5/2		2.5Y 6/4	
45-50	2.5Y 5/4		2.5Y 6/4	
50-55	2.5Y 5/4		2.5Y 6/4	
55-60	2.5Y 5/4		2.5Y 6/2	2.5Y 5/6
60-65	2.5Y 5/4	2.5Y 5/2	2.5Y 6/2	2.5Y 5/6
65-70	2.5Y 4/4	10YR 5/6	2.5Y 6/2	2.5Y 5/6 + 2.5Y 4/2
70-75	2.5Y 5/2		2.5Y 5/4	2.5Y 5/6
75-80	2.5Y 4/2		10YR 5/4	2.5Y 5/4
80-85	2.5Y 4/2		10YR 5/2	
85+	2.5Y 4/2		10YR 5/2	

c) Photograph of core

Note presence of concretions - ferromanganiferous dark brown nodules(upper) and ferrous nodules (lower).



d) E_h and pH measurements

Depth (cm)	Core 1 E_h(mV)	pH	Core 2 E_h(mV)	pH
0-5	420	5.24	450	5.66
5-10	436	5.24	444	5.67
10-15	390	5.68	400	5.23
15-20	382	5.93	426	5.20
20-25	388	6.35	405	4.92
25-30	389	6.20	409	5.53
30-35	381	6.05	415	5.24
35-40	387	6.06	376	5.90
40-45	409	6.26	371	6.12
45-50	400	6.27	387	6.13
50-55	385	6.05	371	6.25
55-60	396	6.03	379	6.11
60-65	398	6.29	391	6.20
65-70	403	6.19	391	5.98
70-75	422	5.92	388	5.97
75-80	435	5.03	373	5.90
80-85	449	5.08	396	5.84
85+	444	5.19	389	5.62

e) 4M HNO_3 - extractable metals

Core 1

Depth (cm)	µg/g (dry-weight) Pb	Zn	Cu	Mn	Cd	%Organic
0-5	53.4	101	11.9	240	.114	18.3
5-10	30.7	88.5	11.2	229	.086	14.1
10-15	21.9	83.3	9.54	206	.090	11.8
15-20	15.5	82.7	7.77	317	.088	8.2
20-25	15.3	79.4	7.29	320	.083	7.6
25-30	17.4	75.2	6.82	626	.088	5.6
30-35	22.0	80.7	7.14	442	.091	3.6
35-40	17.6	71.2	7.49	428	.081	4.0
40-45	20.0	75.2	8.32	332	.079	3.4
45-50	18.5	71.9	9.02	199	.070	4.3
50-55	18.8	70.5	8.85	216	.062	2.7
55-60	17.1	67.1	10.3	123	.098	5.4
60-65	15.7	62.1	12.4	113	.081	5.4
65-70	15.6	57.3	8.8	151	.082	2.9
70-75	13.7	52.1	10.1	100	.076	2.9
75-80	11.8	46.5	13.3	76	.079	5.6
80-85	5.4	30.4	11.2	76	.053	2.2
85+	8.6	33.1	10.9	70	.049	2.1

Core 2

Depth (cm)	µg/g (dry-weight) Pb	Zn	Cu	Mn	Cd	%Organic
0-5	42.4	84.4	10.2	230	0.123	22.2
5-10	35.0	85.0	10.2	240	0.109	12.2
10-15	30.1	102.4	10.3	527	0.106	8.6
15-20	20.3	75.7	6.98	488	0.091	4.1
20-25	21.4	72.2	7.31	423	0.099	3.1
25-30	29.0	68.0	7.88	421	0.094	3.3
30-35	18.9	60.9	8.80	317	0.088	3.5
35-40	15.6	44.8	8.29	173	0.061	3.6
40-45	19.9	56.9	12.4	167	0.059	3.1
45-50	20.5	61.0	13.6	186	0.046	3.6
50-55	22.2	58.9	15.2	188	0.072	3.1
55-60	18.8	54.5	14.7	164	0.081	3.1
60-65	14.9	51.0	16.2	147	0.070	2.7
65-70	14.1	42.7	12.2	210	0.076	2.1
70-75	9.52	29.0	13.5	88	0.057	2.6
75-80	10.3	34.2	11.7	74	0.060	2.2
80-85	9.99	37.4	13.0	76	0.037	2.1

f) 0.04M EDTA(pH6) -extractable metals (Core1)

Depth (cm)	µg/g (dry-weight) Pb	Zn	Cu	Mn	Cd
0-5	31.9	20.2	3.8	108	0.091
5-10	21.3	12.7	4.9	99	0.061
10-15	10.2	4.1	3.3	67	0.043
15-20	7.2	4.7	2.7	78	0.048
20-25	4.5	2.9	2.0	105	0.037
25-30	6.5	5.3	2.5	339	0.068
30-35	5.5	2.1	1.8	155	0.04
35-40	3.7	1.4	1.3	76	0.026
40-45	6.4	1.9	2.2	77	0.015
45-50	5.8	1.7	2.4	39	0.029
50-55	6.9	1.9	3.0	41	0.035
55-60	8.4	1.8	2.5	21	0.044
60-65	8.5	2.2	3.1	12	0.048
65-70	5.0	1.5	2.2	21	0.02
70-75	5.7	1.7	1.9	7.7	0.028
75-80	5.3	1.5	1.7	2.5	0.033
80-85	5.0	0.97	1.6	2.0	0.017

Chapter 6

6.1 Main Divide Peat - Total Metals

Depth (cm)	µg/g (dry-weight) Pb	Zn	Cu	Cd	Mn	Ca
0-2	12.9	14.5	4.1	0.23	70.5	2464
2-4	6.4	11.9	3.6	0.20	44.7	2010
4-6	12.5	13.0	3.3	0.098	30.1	1434
6-8	14.6	11.7	3.1	0.34	47.8	1072
8-10	16.5	13.5	3.5	0.30	20.6	1264
10-12	16.2	10.0	2.9	0.16	49.9	1351
12-14	10.3	7.7	3.3	0.25	17.7	1282
14-16	10.1	7.9	4.6	0.10	4.8	1261
16-18	8.7	6.9	2.5	0.052	3.1	1298
20-22	5.6	3.7	2.3	0.042	2.5	220
22-24	4.3	7.6	3.2	0.069	4.1	621
24-26	3.3	6.2	2.6	0.091	5.4	567
26-28	5.0	4.1	2.2	0.15	4.6	719
28-30	6.5	2.9	2.1	0.23	2.9	646
30-32	4.1	2.7	1.7	0.24	4.5	619
32-34	3.5	3.7	3.4	0.083	3.9	351
34-36	5.0	2.9	3.1	0.12	3.7	740
36-38	4.5	3.1	3.8	0.22	3.9	784
38-40	5.0	1.9	2.6	0.13	3.2	646
40-42	3.4	2.0	2.1	0.19	2.7	583

6.2 Whites Bridge Peat - Total Metals

Depth (cm)	µg/g (dry-weight) Pb	Zn	Mn	Cd	Ca	Cu
0-2	13.5	22.7	222	0.21	1919	2.1
2-4	17.5	21.3	178	0.13	1801	4.6
4-6	12.8	25.7	371	0.12	1813	4.8
6-8	19.5	15.0	195	0.24	680	3.8
8-10	13.9	17.9	160	0.23	1221	4.3
10-12	8.2	10.2	68	0.20	571	1.4
12-14	3.5	4.3	26	0.11	591	4.2
14-16	4.6	6.3	9.9	0.15	541	7.0
16-18	6.2	5.5	7.6	0.14	722	5.0
18-20	3.4	4.8	6.0	0.23	627	4.4
20-22	4.8	4.8	6.7	0.096	703	4.6
22-24	4.6	2.9	5.1	0.34	710	3.0
24-26	3.5	3.2	4.2	0.16	543	4.5
26-28	6.1	2.8	4.3	0.13	699	3.9
28-30	4.4	2.7	4.4	0.099	617	4.7
30-32	4.8	2.4	4.9	0.099	603	4.0
32-34	4.2	1.9	3.0	0.12	541	3.8
34-36	4.9	2.2	3.3	0.13	559	3.8
36-38	6.8	1.9	5.8	0.20	495	4.4
38-40	6.3	1.6	3.9	0.19	512	3.3

6.3 Craigieburn Peat - Total Metals

Depth (cm)	µg/g (dry-weight) Pb	Zn	Cu	Mn	Cd	Ca
0-2	9.6	23.9	6.2	405	0.32	733
2-4	14.1	23.3	4.1	303	0.36	1145
4-6	17.1	24.2	4.2	544	0.26	969
6-8	11.4	20.1	4.7	302	0.22	1058
8-10	9.4	16.6	4.0	193	0.18	948
10-12	4.5	18.0	3.8	198	0.27	1107
12-14	2.8	15.3	5.6	107	0.31	888
14-16	1.5	17.0	5.2	168	0.24	685
16-18	1.5	12.9	2.4	94	0.32	820
18-20	2.4	12.4	4.3	82	0.19	731
20-22	1.9	8.5	2.5	58	0.17	562
22-24	2.5	9.2	8.2	55	0.15	611
24-26	3.2	6.1	8.0	42	0.17	544
26-28	1.8	6.7	8.5	29	0.20	463
28-30	1.9	5.3	6.9	31	0.13	508
30-32	2.9	5.5	9.5	33	0.13	521
32-34	3.9	6.2	8.5	32	0.11	609
34-36	4.1	2.8	5.6	25	0.22	479
36-38	7.5	12.1	7 .0	24	0.16	502

6.4 Field measurements

a) Organic content and pH of Whites Bridge bog

Depth(cm)	% Organic	pH
0-2	95.3	3.60
2-4	92.8	3.64
4-6	92.8	3.65
6-8	90.9	3.76
8-10	91.2	3.62
10-12	90.3	3.45
14-16	90.3	3.43
16-18	93.5	3.44
18-20	92.2	3.48
20-22	89.2	3.52
22-24	88.2	3.54
24-26	87.2	3.58
26-28	85.1	3.51
28-30	87.4	3.58
30-32	90.2	3.61
32-34	87.0	3.63
34-36	85.6	3.58
36-38	84.5	3.63
38-40	86.0	3.55

b) E_h of all bogs

Depth (cm)	E_h(V) WB	MD	CB
0	.623	.475	.700
5	.520	.430	.605
10	.250	.133	.275
15	.227	.105	.271
20	.216	.083	.266
25	.209	.070	.265
30	.196	.048	.254
35	.191	.033	.252
40	.183	.012	.250